On the kinetics of boron nitride CVD from BF3-NH3-Ar : 2 - Influence of the precursor composition and chemical mechanisms

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ON THE KINETICS OF BORON NITRIDE CVD FROM BF_3-NH_3-Ar : 2 - INFLUENCE OF THE PRECURSOR COMPOSITION AND CHEMICAL MECHANISMS.

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ABSTRACT

An experimental study is used to assess the kinetics of boron nitride CVD from BF_3-NH_3-Ar mixtures and the influence of the initial gas phase composition on the transition from mass transfer to chemical reaction rate-controlled processes. The extension of the chemical reaction rate-controlled domain in the coordinates P_{BF_3}-P_{NH_3} is determined for three temperatures (1250, 1350 and 1450 K) and a given total flow rate (Q_{tot}= 119 sccm). In the surface reaction controlled regime, the kinetic laws are established ; apparent partial reaction orders with respect to BF_3, NH_3, Ar and HF are given for various conditions. The apparent partial reaction orders with respect to Ar and NH_3 are nil and those with respect to BF_3 and HF are depending on temperature and total pressure. Finally, reactional mechanisms, according to the kinetic laws and chemical analyses performed on deposits obtained in the

domains corresponding to these laws, are proposed to explain the chemical processes of BN deposition. One mechanism assumes the occurrence of the BF_3:NH_3 adduct in the gas phase at low temperatures ; the other, at higher temperatures, is based on the hypothesis that NH_3 is preferentially adsorbed on the substrate and reacts with the BF_3 present in the gas phase.

KEY WORDS : Boron Nitride, CVD, Kinetics, BF_3, NH_3, Reactionnal mechanisms

1- INTRODUCTION

Chemically vapour deposited boron nitride exhibits very interesting physical and chemical properties which are known to highly depend on the conditions of synthesis (i. e. electrical properties and sensivity to the moisture [1]).

Whatever the gas mixture used as precursor of BN, the change of the experimental parameters (i. e. pressure, temperature and total flow rate) induces important variations in density, morphology, structure of the deposits and stablity to moisture [2-8]. Moreover, the oxygen plays an important catalytic role in the "graphitization process" of turbostratic boron nitride [9]. The influence of the initial gas phase composition on the nature of the deposit was approached in previous studies [3,4,10] that described the variation of morphology and growth rate as a function of the ratio NH_3/BCl_3.

The companion article (part 1) [11] detailed the influence of the main CVD parameters on the BN deposition kinetics, in the BF_3-NH_3-Ar system. Moreover, the initial composition of the gaseous precursor defined by the α ratio of the partial pressures of NH_3 and BF3 : $\alpha = P_{NH_3}/ P_{BF_3}$ seemed to be a

critical parameter. Indeed, the extension of the chemically controlled deposition domain was found to be very different for two distinct α values.
The purpose of the present contribution is : (i) to study more precisely the influence of the α-parameter on the transition from mass transfer to chemical reaction rate controlled processes and on the chemical composition of the deposit and(ii) to determine, in the different thermally activated domains, the kinetic laws and to propose an approach of the chemical mechanisms.

2- RESULTS

2.1- Influence of the initial gas phase composition on the transition between physical and chemical rate control.

The influence of the initial composition of the gas phase upon the transition between the diffusion-controlled and the reaction-controlled regimes is studied following the method developed in part 1 [11]. The experiments were performed by using the previously described apparatus for three temperatures (1250, 1350 and 1450 K) with an α ratio ranging from 0.5 to 5, the dilution ratio β ($\beta = P_{Ar} / P_{NH_3}+P_{BF_3}$) and the total flow rate (Q_{tot}=110-120 sccm) being maintained constant.

Under these conditions, the variations of the growth rate, as a function of the total reactive pressure (defined as $P_{tr} = P_{NH_3}+ P_{BF_3}$), and the corresponding total pressure ($P= P_{Ar}+P_{tr} = (1+\beta) P_{tr}$) are shown in figures 1 to 3. For the three temperatures, the curves exhibit two distinct parts. At low pressures, the growth rate increases with P_{tr} and then remains rather constant or slightly decreases. A transition pressure range, located around the maximun of growth rate-total reactive pressure curve, is defined for each α

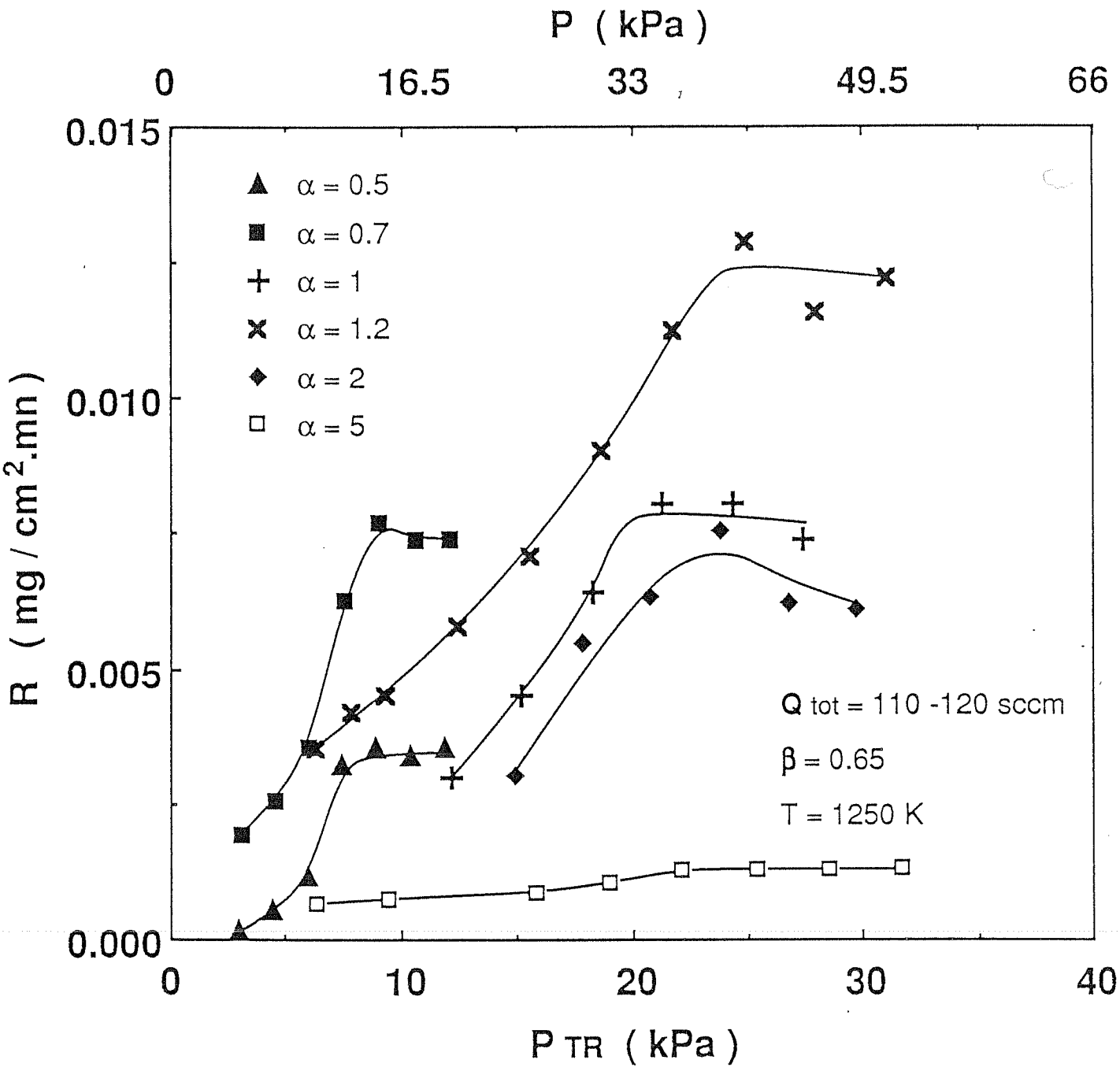

Fig.1 : Variations of BN growth rate with total pressure P and total reactive pressure P_{tr} for T= 1250 K and various α values

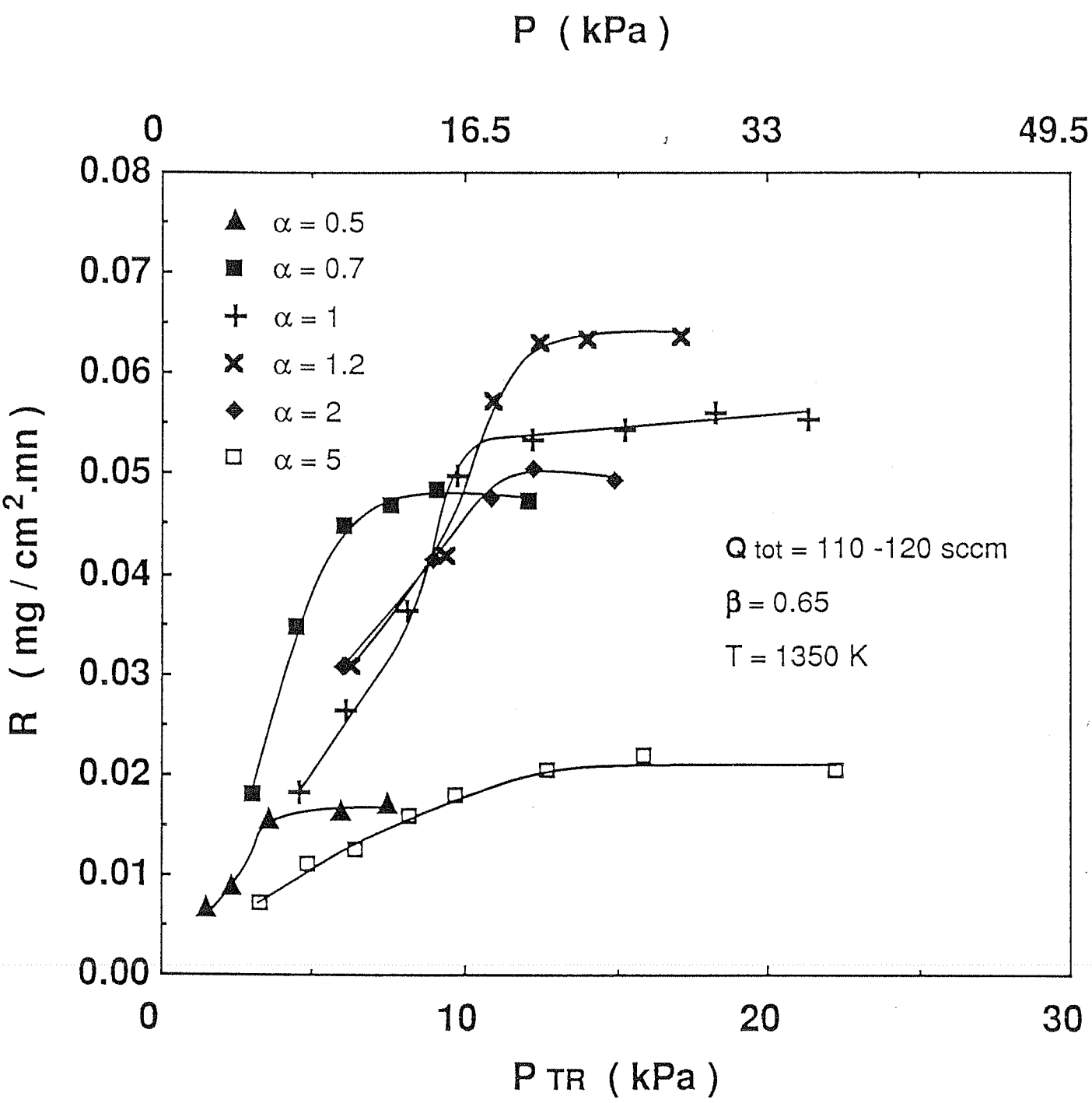

Fig.2 : Variations of BN growth rate with total pressure P and total reactive pressure P_{tr} for T= 1350 K and various α values

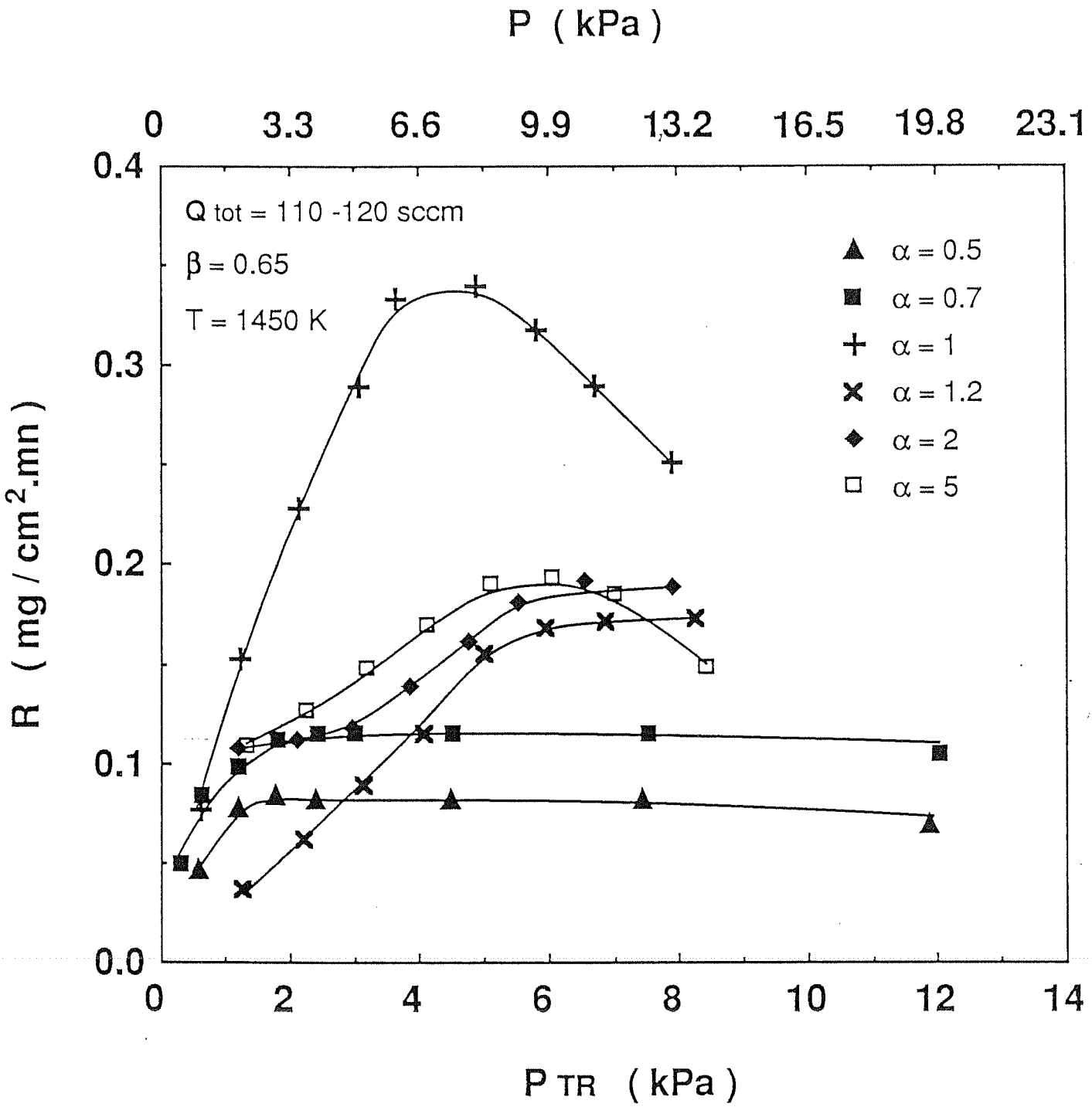

Fig.3 : Variations of BN growth rate with total pressure P and total reactive pressure P_{tr} for T= 1450 K and various α values

ratio at a given temperature, total flow rate and dilution ratio. The (α,P_{tr}) couples are then plotted in the plane (P_{BF_3},P_{NH_3}). The interest of such a representation mode is detailed in appendix. The plots established for T= 1250 K (Fig. 4) define the limit between two domains. In the low pressures domain, the deposition rate is limited by chemical reaction kinetics. For higher total reactive pressures, mass transfers become the limiting phenomena of the deposition process. Total reactive pressure values which induce the transition between these two regimes are constant for $\alpha \geq 1$. For $\alpha \leq 1$, the transition pressure decreases with α. The chemical rate-controlled domain is narrowed when BF_3 becomes the major species in the initial gaseous phase.

As the temperature is increased, the extension of the reaction-controlled domain decreases but exhibits the same shape, (Fig. 5). This is in accordance with the tendencies determined from the (P,T) plots in [11], and with the general trend in CVD processes which is to favor physical rate limitation by increasing temperature [10-13].

2.2- Apparent reaction orders

When the chemical reactions are the rate-controlling steps in the CVD process, it is of interest to assess experimental apparent reaction orders with respect to the reactant species (NH_3 and BF_3) introduced in the gas phase. The influences of HF (the main gas product) and Ar (used as dilution species) must be also studied in order to derive complete kinetic laws and to suggest chemical mechanisms for the deposition process. In the case of HF (the main reaction product), the added partial pressure is rather important with respect to total reactive pressure P_{tr}.

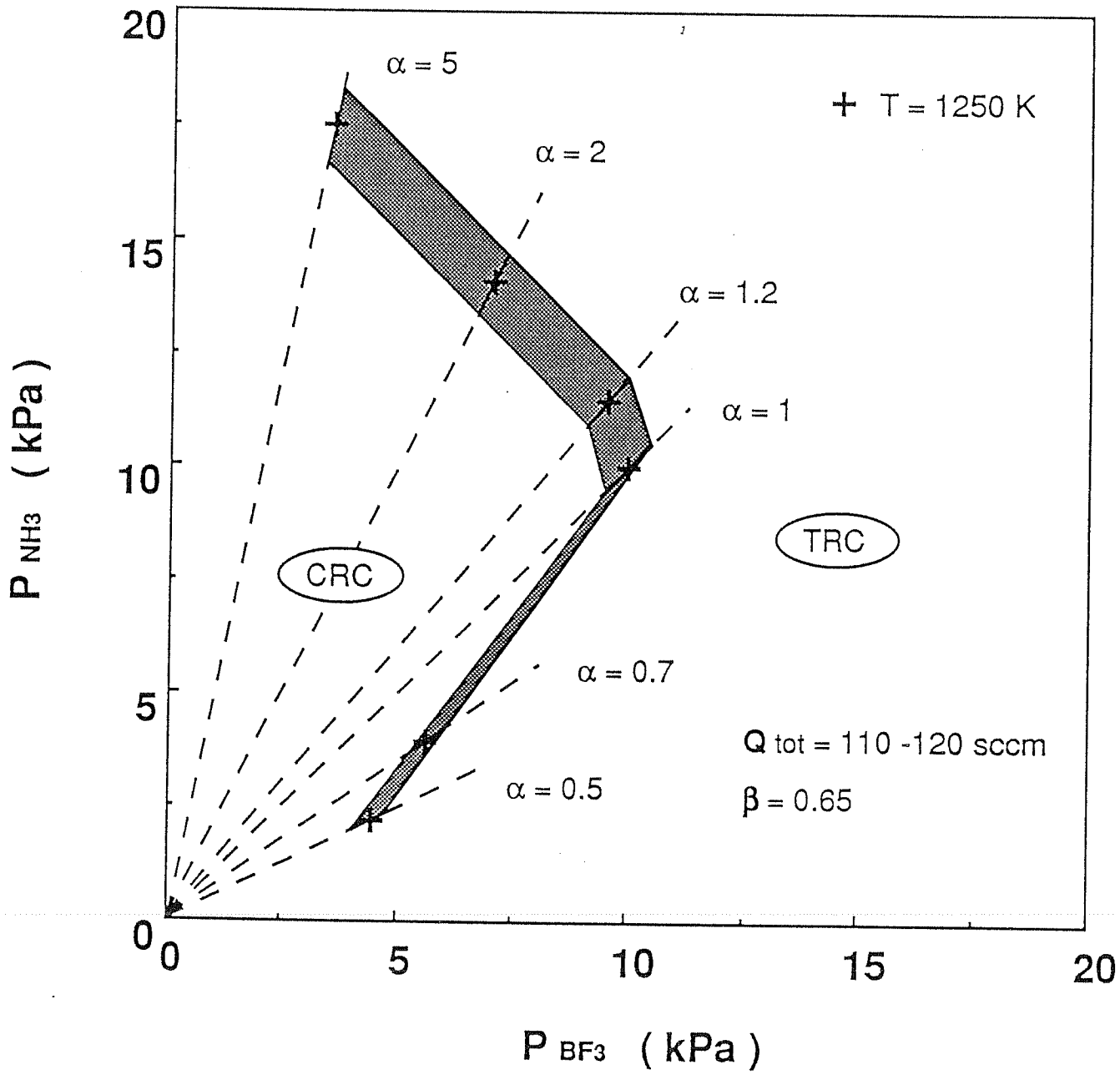

Fig.4 : Transition zone in terms of P_{BF_3} and P_{NH_3} between transfer rate control (TRC) at high pressures and chemical rate control (CRC) at low pressures of the BN deposition process, for T= 1250 K and various compositions of the initial gaseous mixture

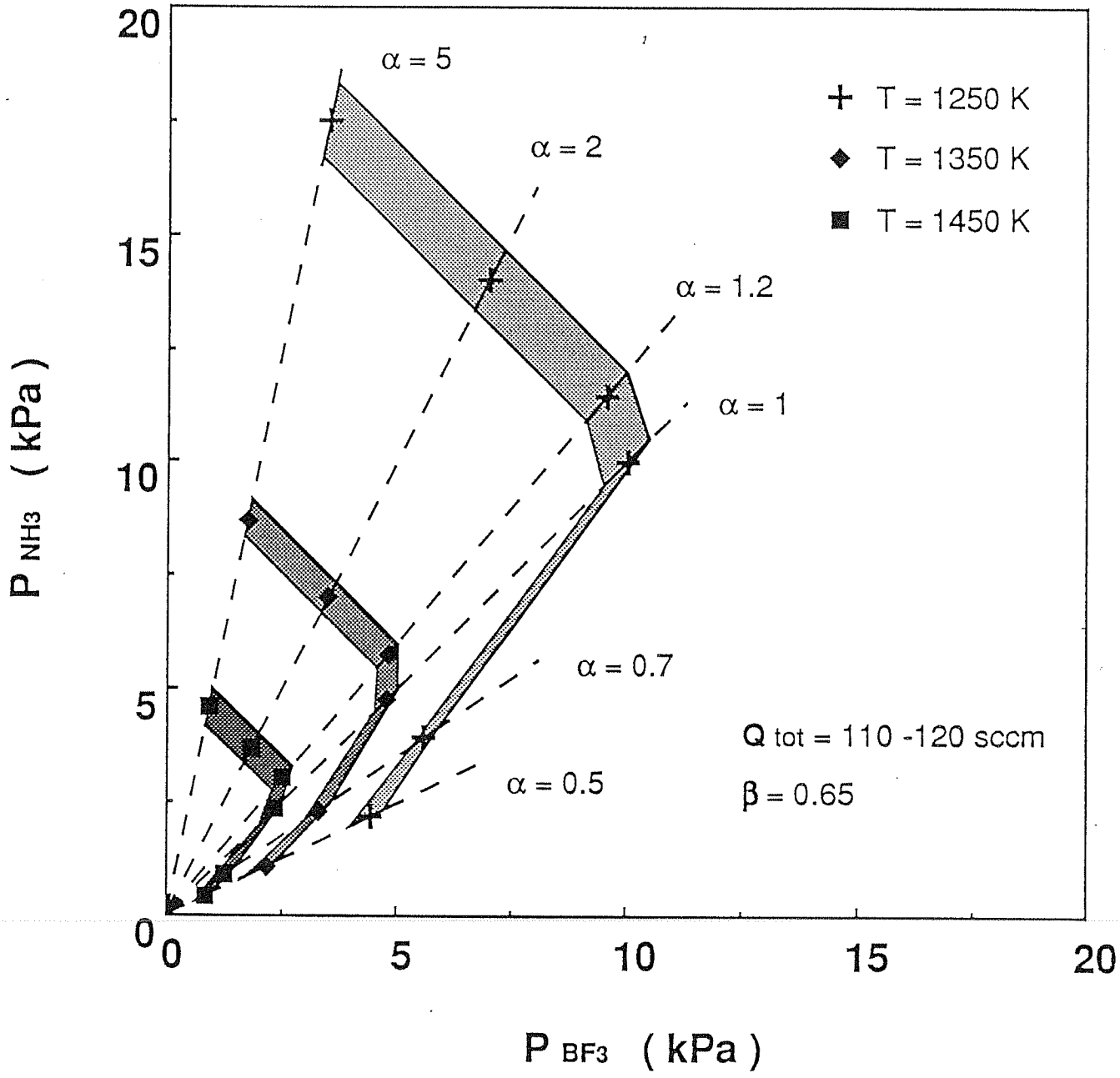

Fig.5 : Transition zone in terms of P_{BF_3} and P_{NH_3} between transfer rate control (TRC) at high pressures and chemical rate control (CRC) at low pressures of the BN deposition process, for T= 1250, 1350 and 1450 K, and various compositions of the initial gaseous mixture

The influence of various partial pressures on the deposition rate of BN was quantitatively studied for three temperatures (1250,1350 and 1450 K) and conditions of total reactive pressure suitably defined according to the conclusions of the last section. In order to determine the apparent reaction order with respect to a species i, the experiments are performed by maintaining constant the flow rates Qj and the partial pressures P_j of all the species j (with $j \neq i$) and by varying the total pressure and the partial flow rate and pressure of the considered species i . The data are shown in figures 6 to 19 as ln R = f (ln P_i) curves. These are found to be straight lines and for HF species the slope n_3 is negative. In order to get a finite value for the growth rate R when P_{HF} is very low, a kinetic law of the following kind can fit with the experimental results :

$$R = \frac{k'_0 \exp(-\mathcal{E}'_a/\Re T)\,[P_{BF_3}]^{n1} \cdot [P_{NH_3}]^{n2} \cdot [P_{Ar}]^{n4}}{1 + (k''_0 \exp(-\mathcal{E}''_a/\Re T)\,[P_{HF}]^{-n3})}$$

where R is the reaction rate (mg/mn.cm^2), k'_0 and k''_0 the pre-exponential factors of the kinetic constants, $\mathcal{E}'_a$ and $\mathcal{E}''_a$ the apparent activation energies, $\Re$ the perfect gas constant, T the temperature, P_i the partial pressure of the species i (with i=1 to 4) and n_i the apparent reaction orders with respect to the reactants (NH_3, BF_3), the product (HF) and the dilution species (Ar).

If $k''_0 \exp(-\mathcal{E}''_a/\Re T)\,[P_{HF}]^{-n3} \ll 1$ (i. e. $[P_{HF}] \approx 0$), this law could be written as :

$$R = k'_0 \exp(-\mathcal{E}'_a/\Re T)\,[P_{BF_3}]^{n1} \cdot [P_{NH_3}]^{n2} \cdot [P_{Ar}]^{n4}$$

On the contrary, when $k''_0 \exp(-\mathcal{E}''_a/\Re T)\,[P_{HF}]^{-n3} >> 1$, the kinetic law becomes :

$$R = k_0 \exp(-(\mathcal{E}'_a-\mathcal{E}''_a)/\Re T)\,[P_{BF_3}]^{n1} \cdot [P_{NH_3}]^{n2} \cdot [P_{HF}]^{n3} \cdot [P_{Ar}]^{n4}$$

or

$$R = k_0 \exp(-E_a/\Re T)\,[P_{BF_3}]^{n1} \cdot [P_{NH_3}]^{n2} \cdot [P_{HF}]^{n3} \cdot [P_{Ar}]^{n4}$$

where k_0 is the pre-exponential factor of the kinetic constant, and $E_a=\mathcal{E}'_a-\mathcal{E}''_a$ the apparent activation energy.

The plots $\ln R = f(\ln P_{BF_3})$, recorded for T= 1450 K and shown in figure 6, exhibit an apparent reaction order $n_1 = 1$. This value is obtained for P_{BF_3} ranging from 0.5 to 2 kPa and two partial pressures of NH_3 (1.5 and 2 kPa). For NH_3, the apparent reaction order n_2 is derived from two different sets of experiments carried out for P_{BF_3} equal to 1 and 0.5 kPa. In both cases it is considered to be zero (Fig. 7).

Data concerning Ar and HF [$0.6 \leq P_{HF} \leq 1.35$ kPa] are shown in figures 8 and 9. As could be expected, the apparent reaction order with respect to argon derived from three different runs in the total pressure range (1-6 kPa), is observed to be zero ($n_4 = 0$). The significant negative value ($n_3 = -3$) of the apparent reaction order with respect to HF suggests the important rôle played by this species in the formation of BN.

As a result, the following kinetic law is proposed for T= 1450 K and the domain of partial pressures defined in figure 9 and 10 :

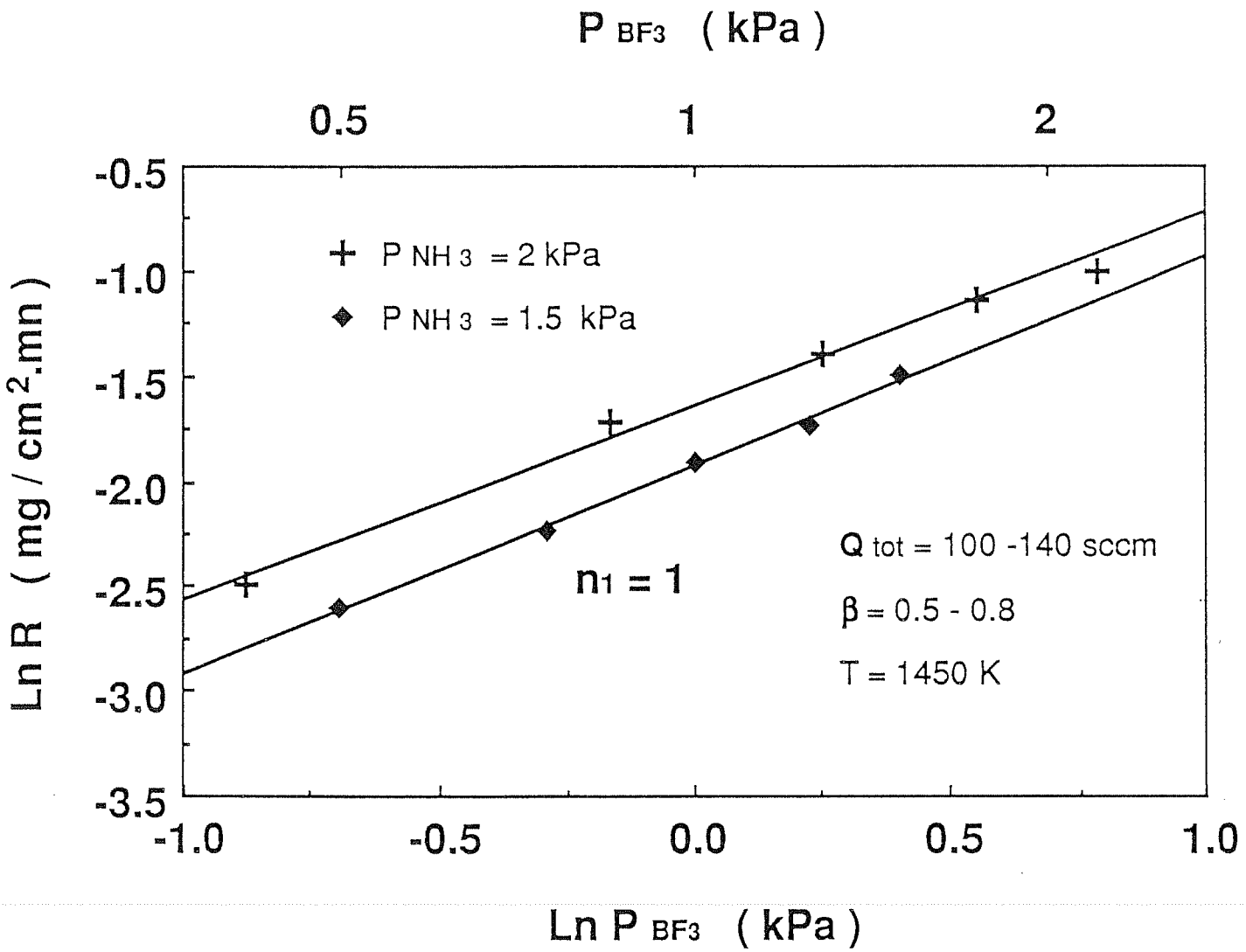

Fig.6 : Variation of BN growth rate with partial pressure of BF_3 for T= 1450 K

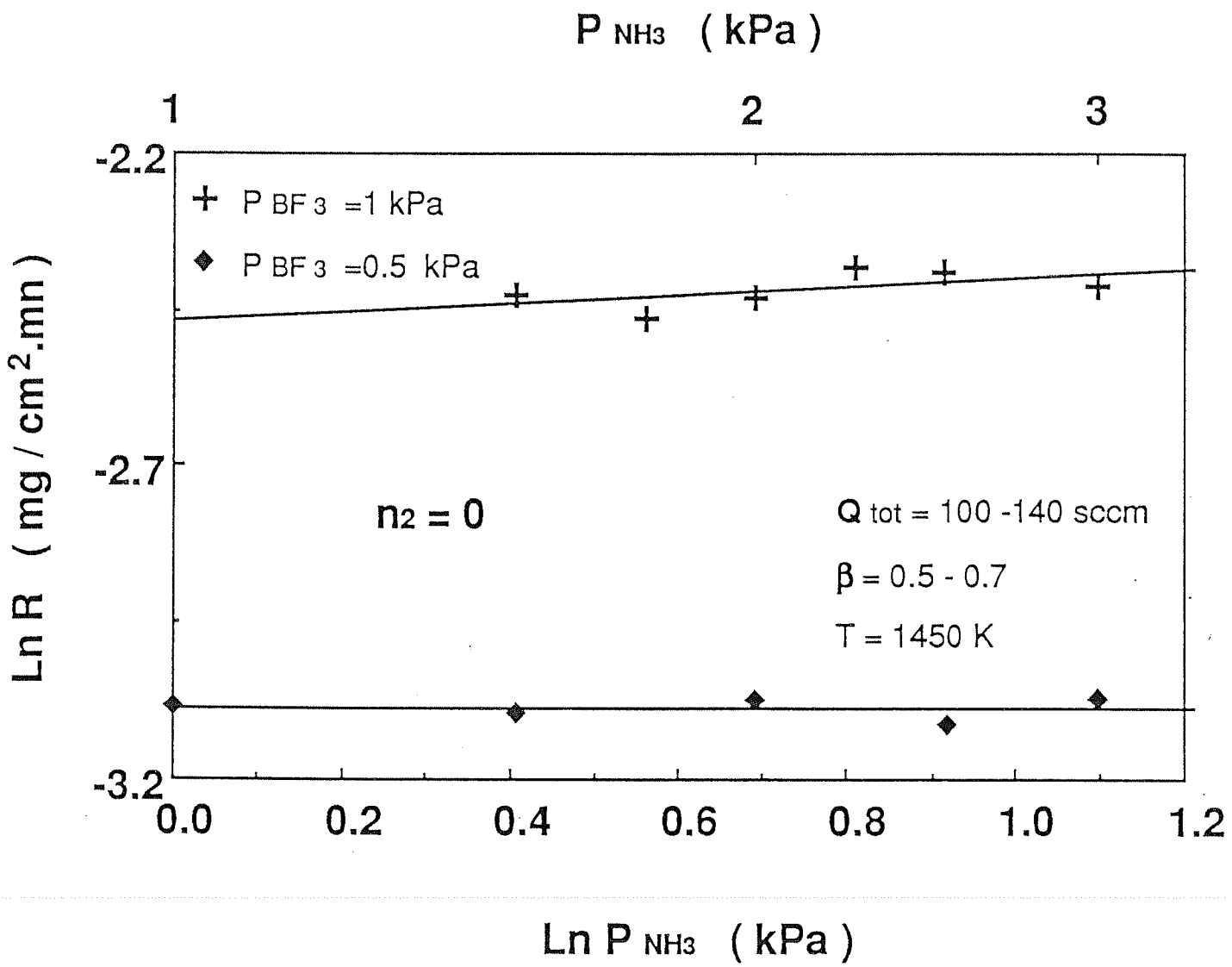

Fig.7 : Variation of BN growth rate with partial pressure of NH_3 for T= 1450 K

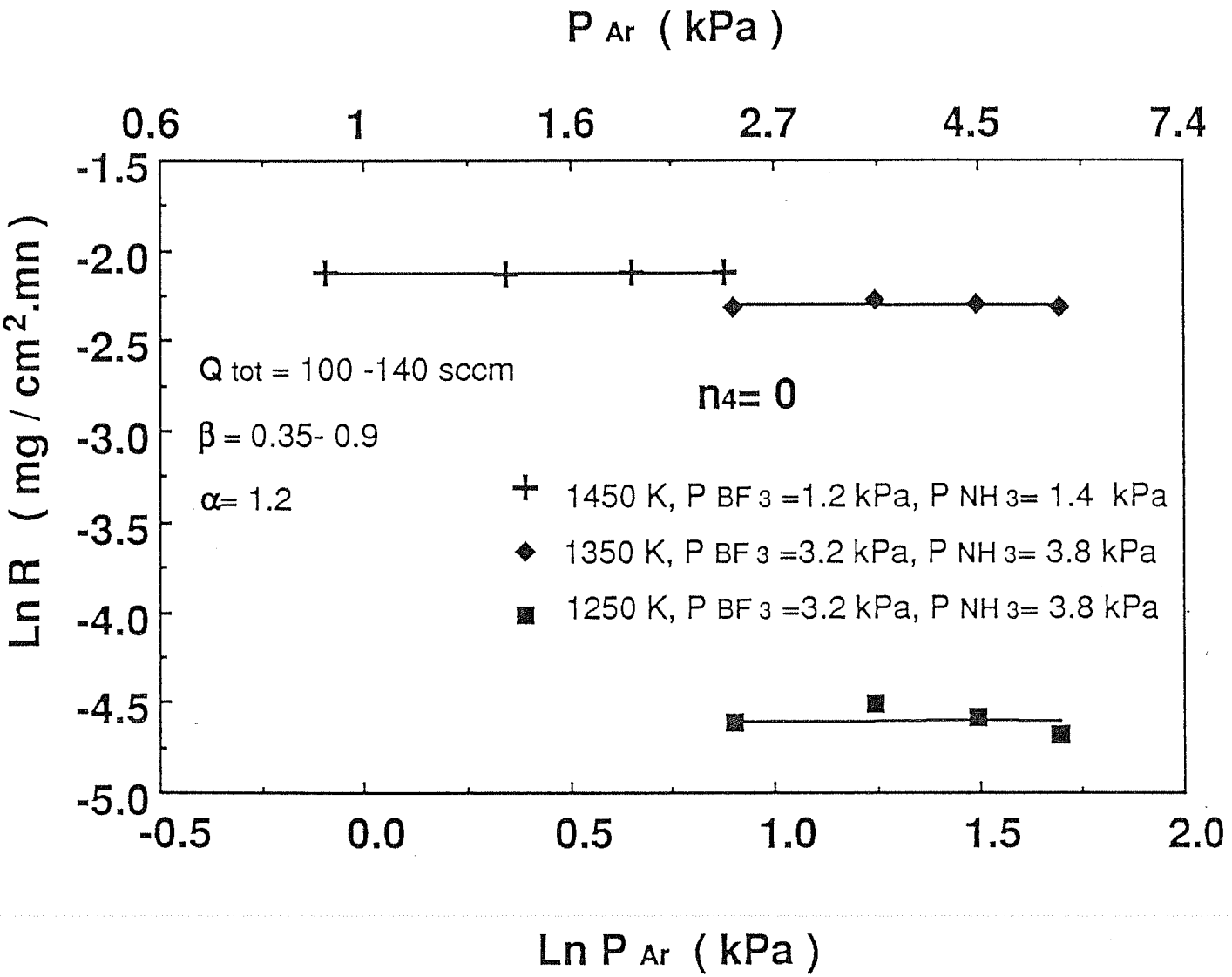

Fig.8 : Variation of BN growth rate with partial pressure of Ar for different temperatures and total reactive pressures

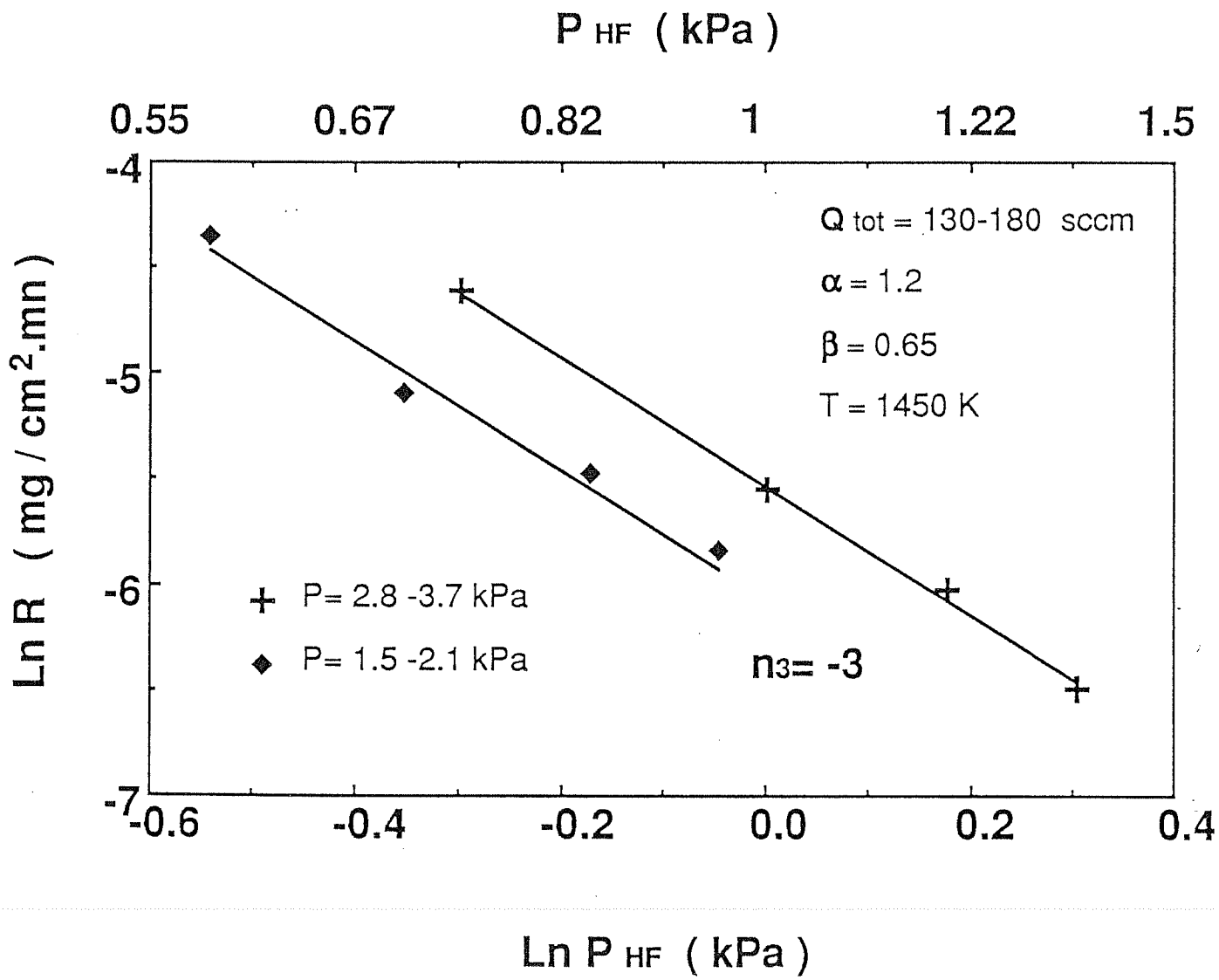

Fig.9 : Variation of BN growth rate with partial pressure of HF for T= 1450

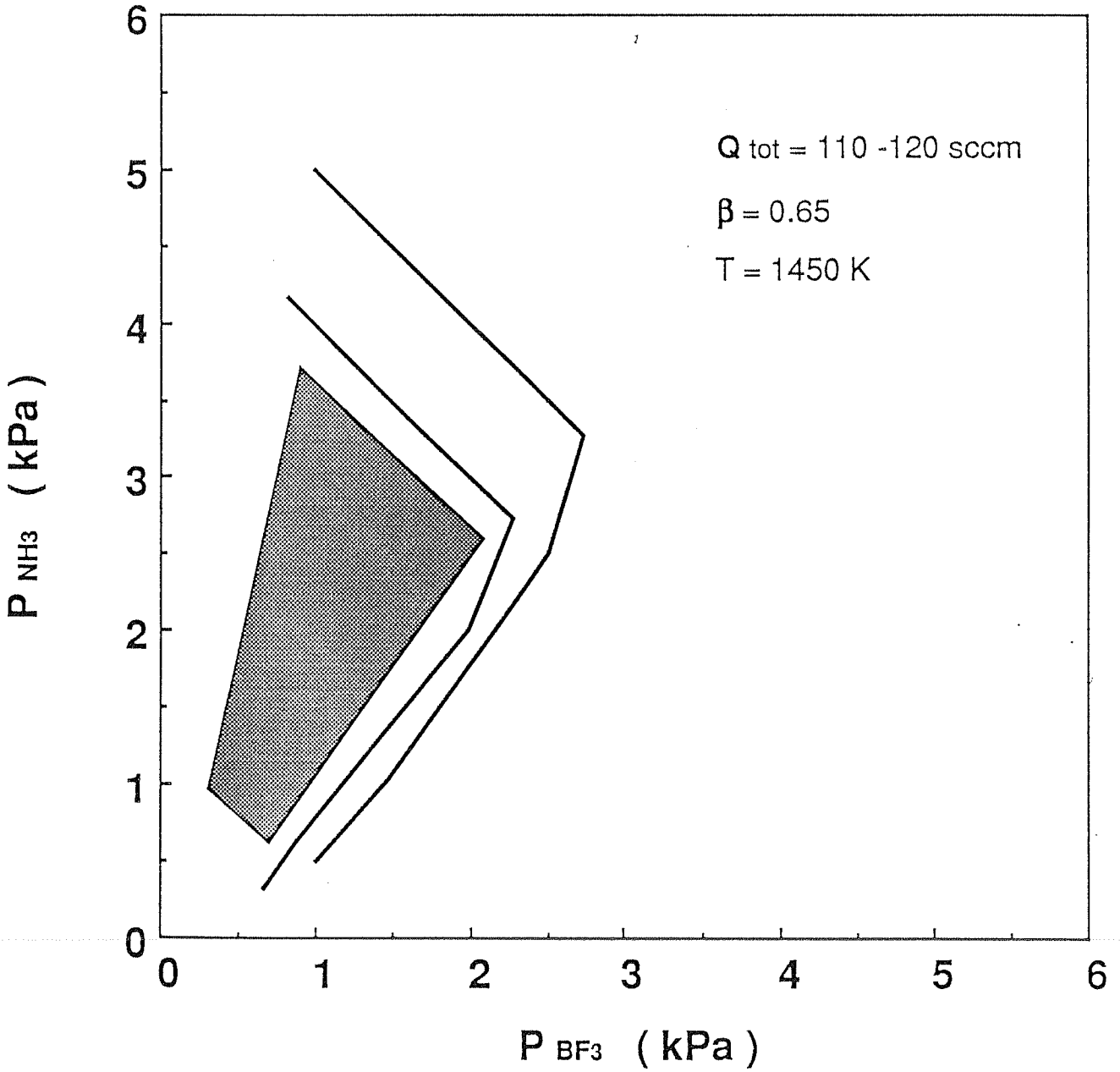

Fig.10 : Domain of validity for the kinetic law A at T= 1450 K

$R = k_0 \exp(-E_a/\Re T) [P_{BF_3}]^1 . [P_{NH_3}]^0 . [P_{HF}]^{-3} . [P_{Ar}]^0$ (Law A)

where $E_a = 290 \pm 15$ kJmol^{-1} [11], $< k_0 > = 1.03.10^{14}$ mg.Pa^2/cm^2.mn

$< k_0 >$ is an average value calculated from all the experimental growth rates obtained in presence of added HF at 1450 K

The data reported for T= 1350 K in figures 8, 11, 12, and 13, give the same partial orders with respect to all the species studied as in the preceding case.

The same kinetic law is proposed for a given domain of partial pressures of BF3 and NH3 (Fig. 14) and $0.55 \leq P_{HF} \leq 1.4$ kPa:

$R = k_0 \exp(-E_a/\Re T) [P_{BF_3}]^1 . [P_{NH_3}]^0 . [P_{HF}]^{-3} . [P_{Ar}]^0$ (Law A)

where $E_a = 290 \pm 15$ kJmol^{-1} [11], $< k_0 > = 6.5.10^{14}$ mg.Pa^2/cm^2.mn

$< k_0 >$ is an average value calculated from all the experimental growth rates obtained in presence of added HF for 1350 K

From the ln R = f (ln P_i) graphs established for T= 1250 K and shown in figures 8 and 15 to 19, it can be seen that the apparent reaction orders with respect to NH_3 and argon are unchanged ($n_2 = n_4 = 0$).

On the other hand, the influences of the partial pressures of BF_3 and HF on the deposition rate of BN are more complex. The data recorded from several runs, show the existence of two distinct partial reaction orders with respect to each species :

- $n_1 = 0$ and $n_3 = -1$
- $n_1 = 1.5$ and $n_3 = -2$

As a consequence, two different kinetic laws depending on the values of partial pressures of BF3 and NH3 (Fig. 20) are proposed :

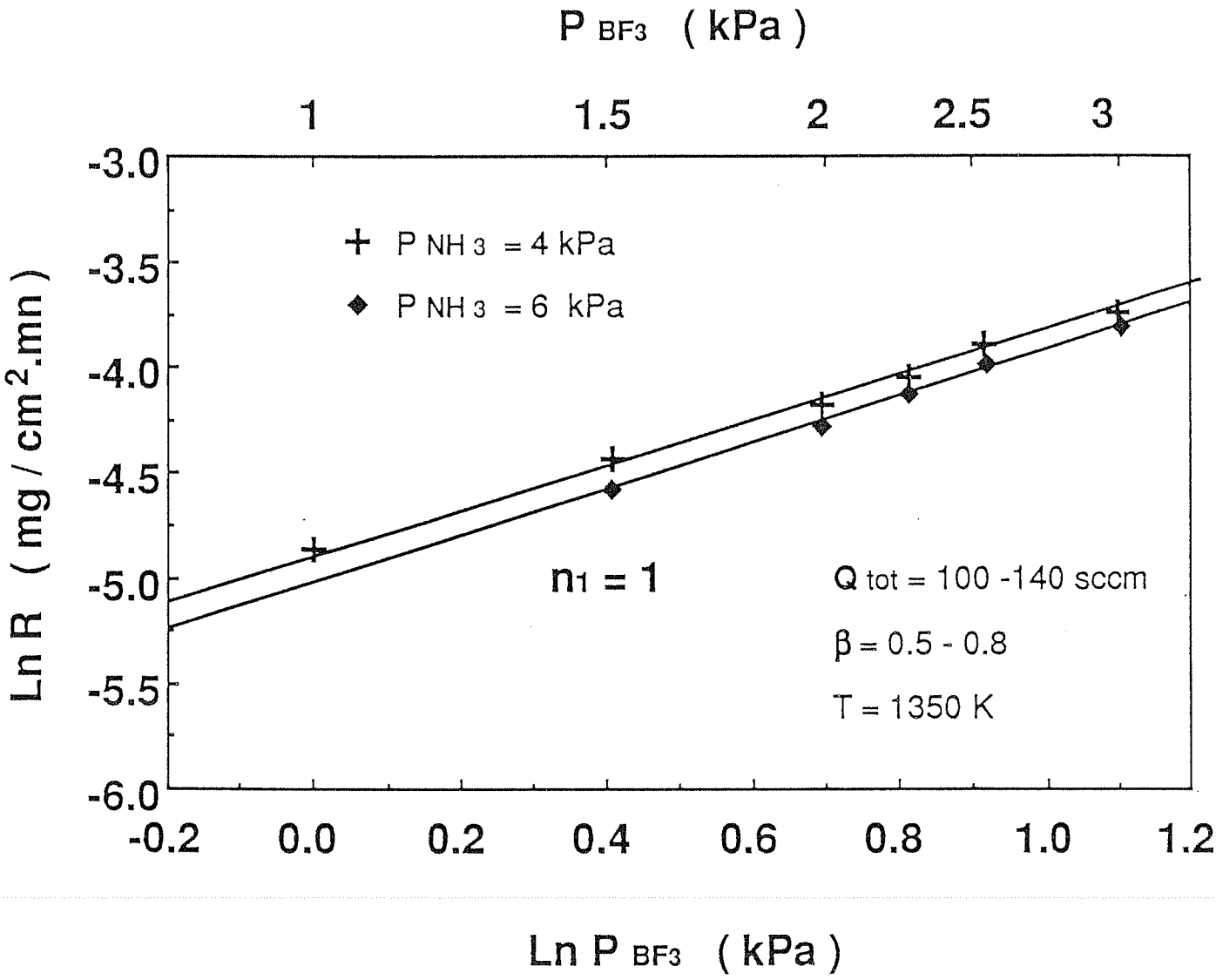

Fig.11 : Variation of BN growth rate with partial pressure of BF_3 for T= 1350 K

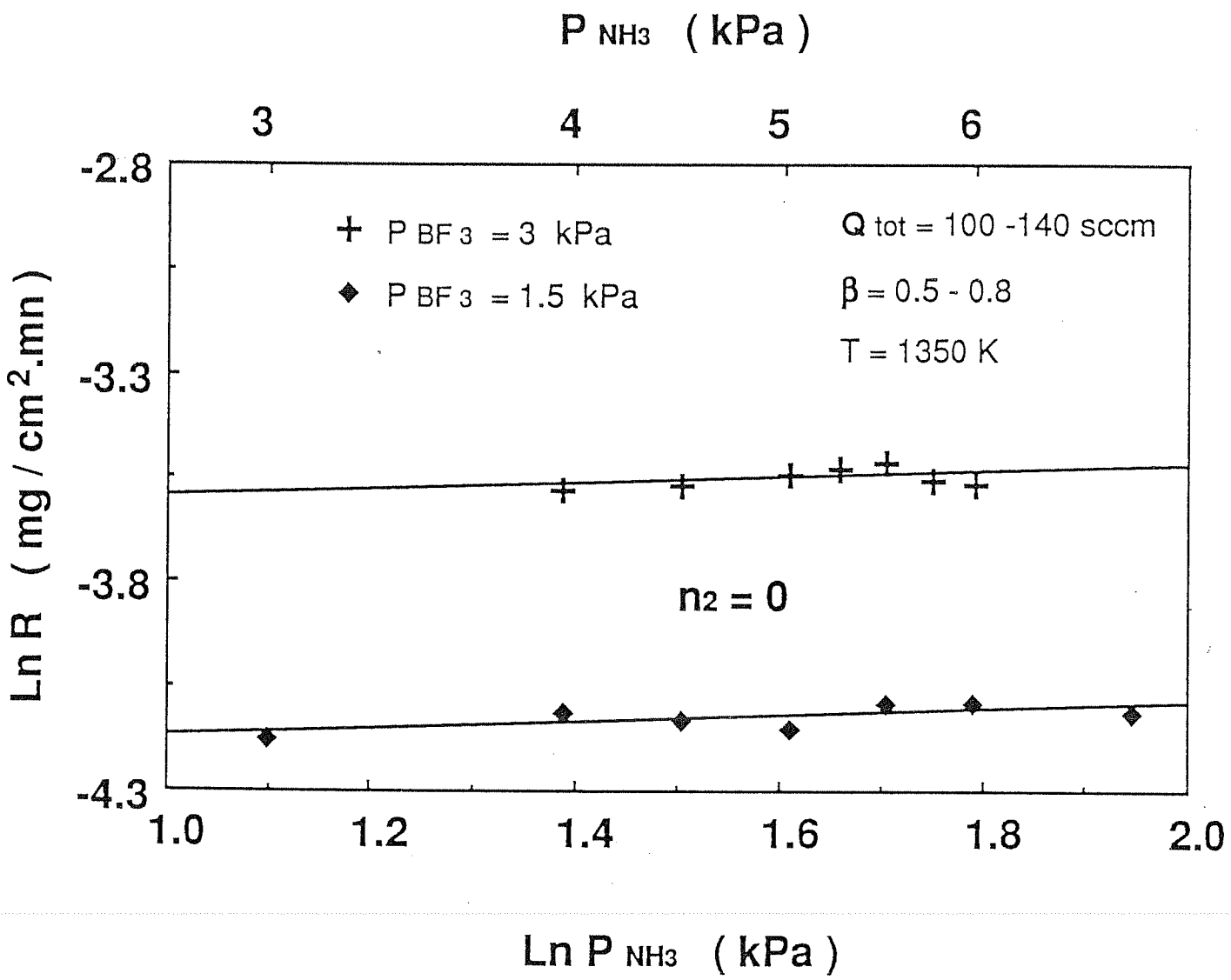

Fig.12 : Variation of BN growth rate with partial pressure of NH_3 for T= 1350 K

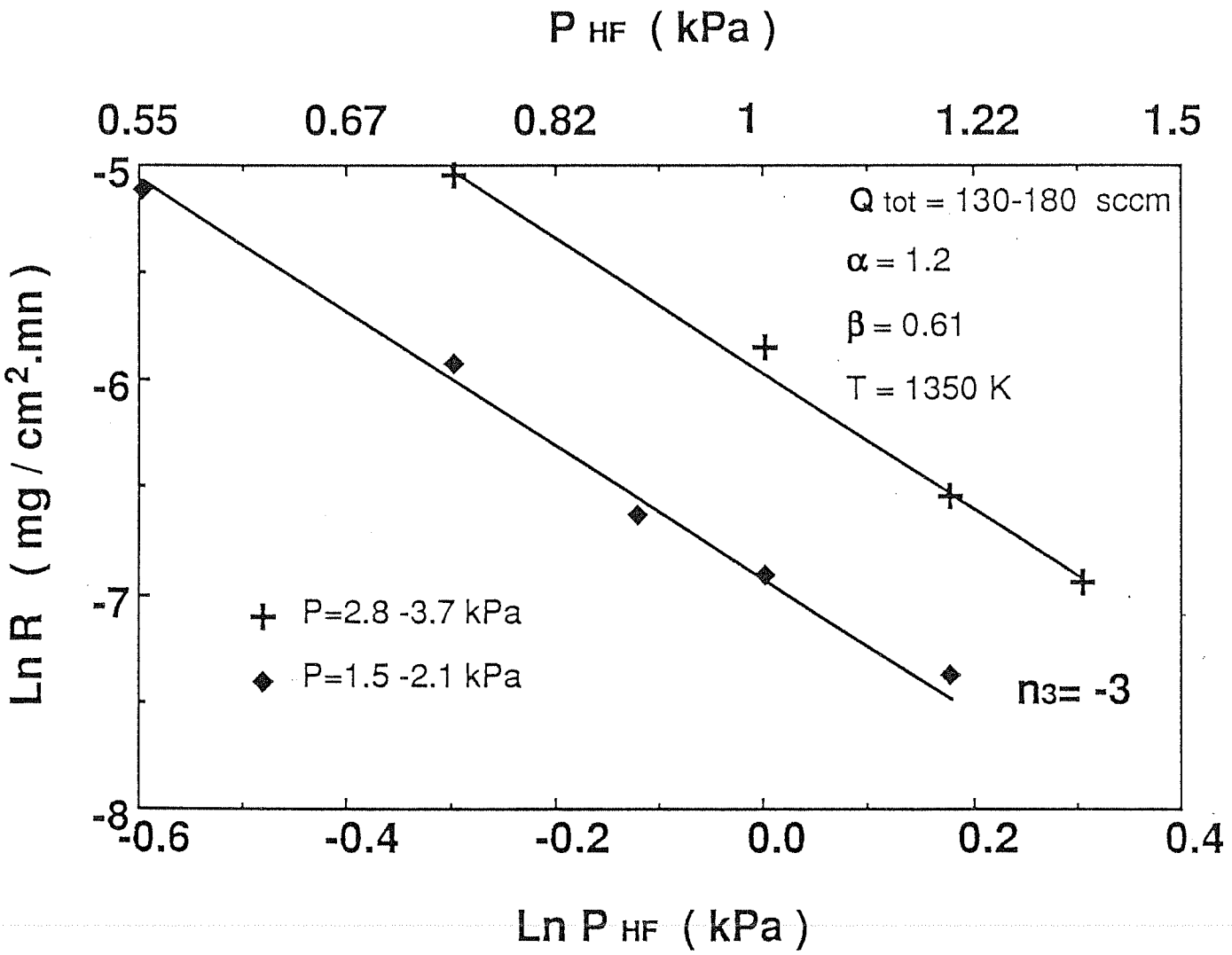

Fig.13 : Variation of BN growth rate with partial pressure of HF for T= 1350 K

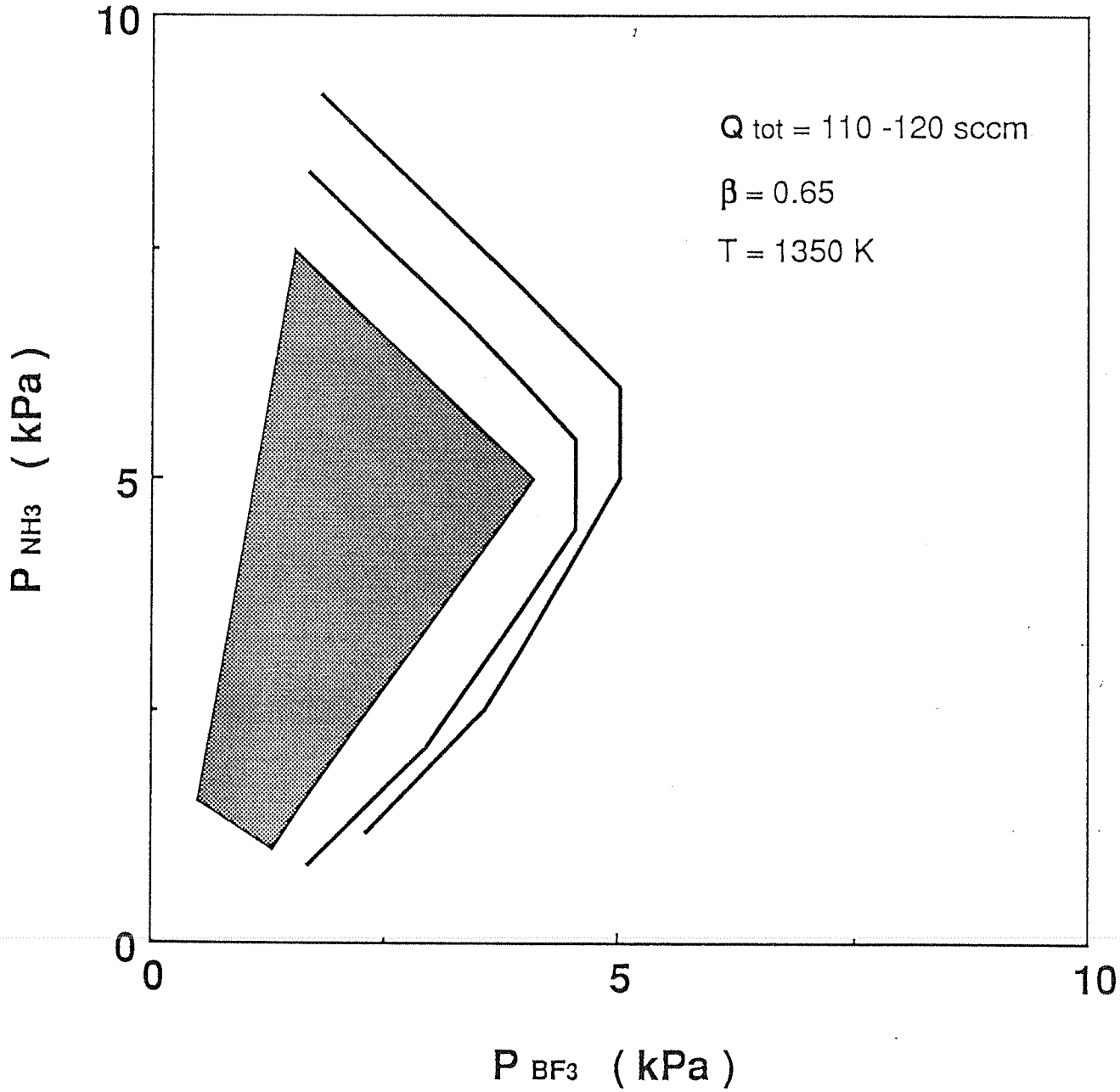

Fig.14 : Domain of validity for the kinetic law A at T= 1350 K

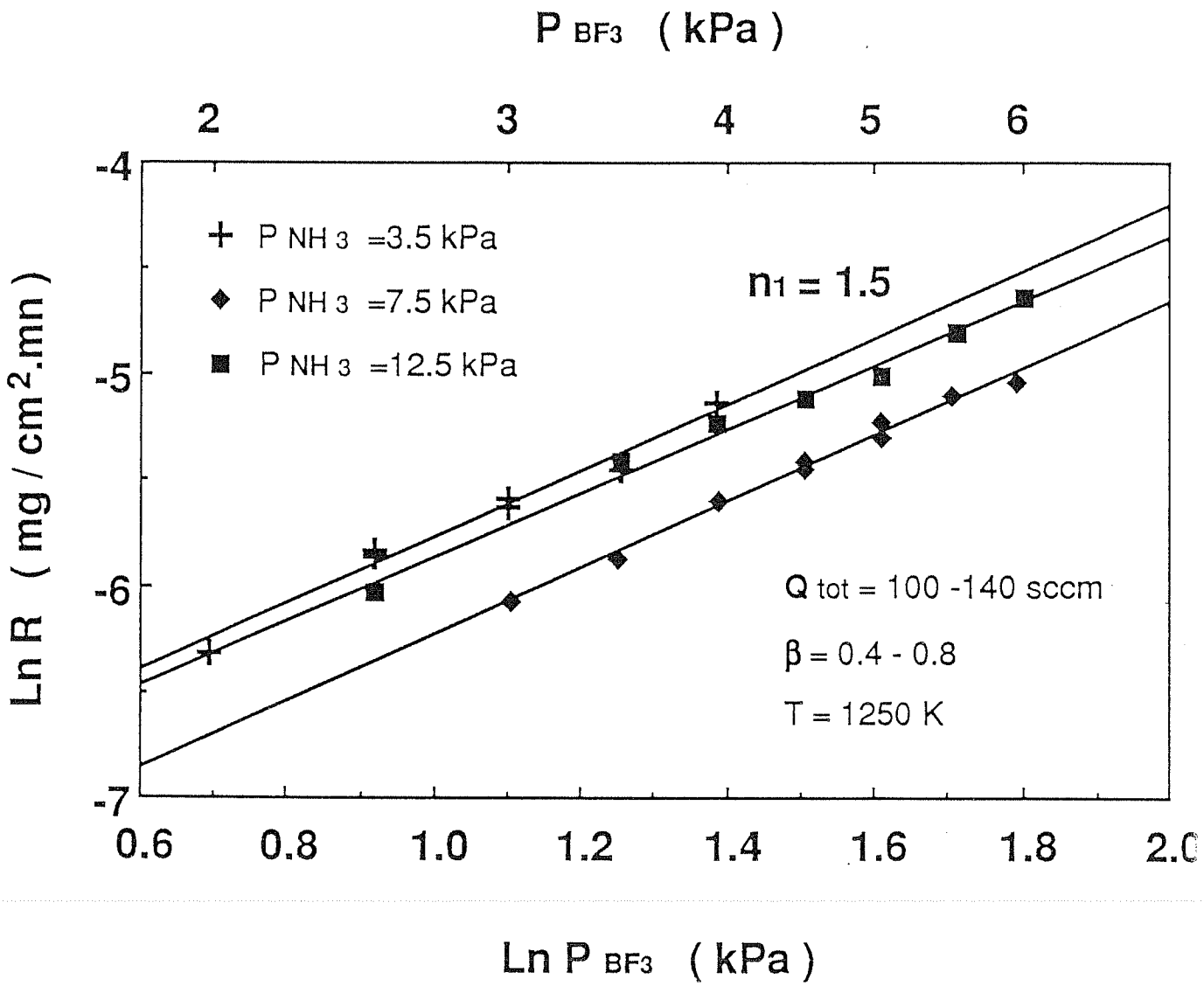

Fig.15 : Variation of BN growth rate with partial pressure of BF_3 for T= 1250 K

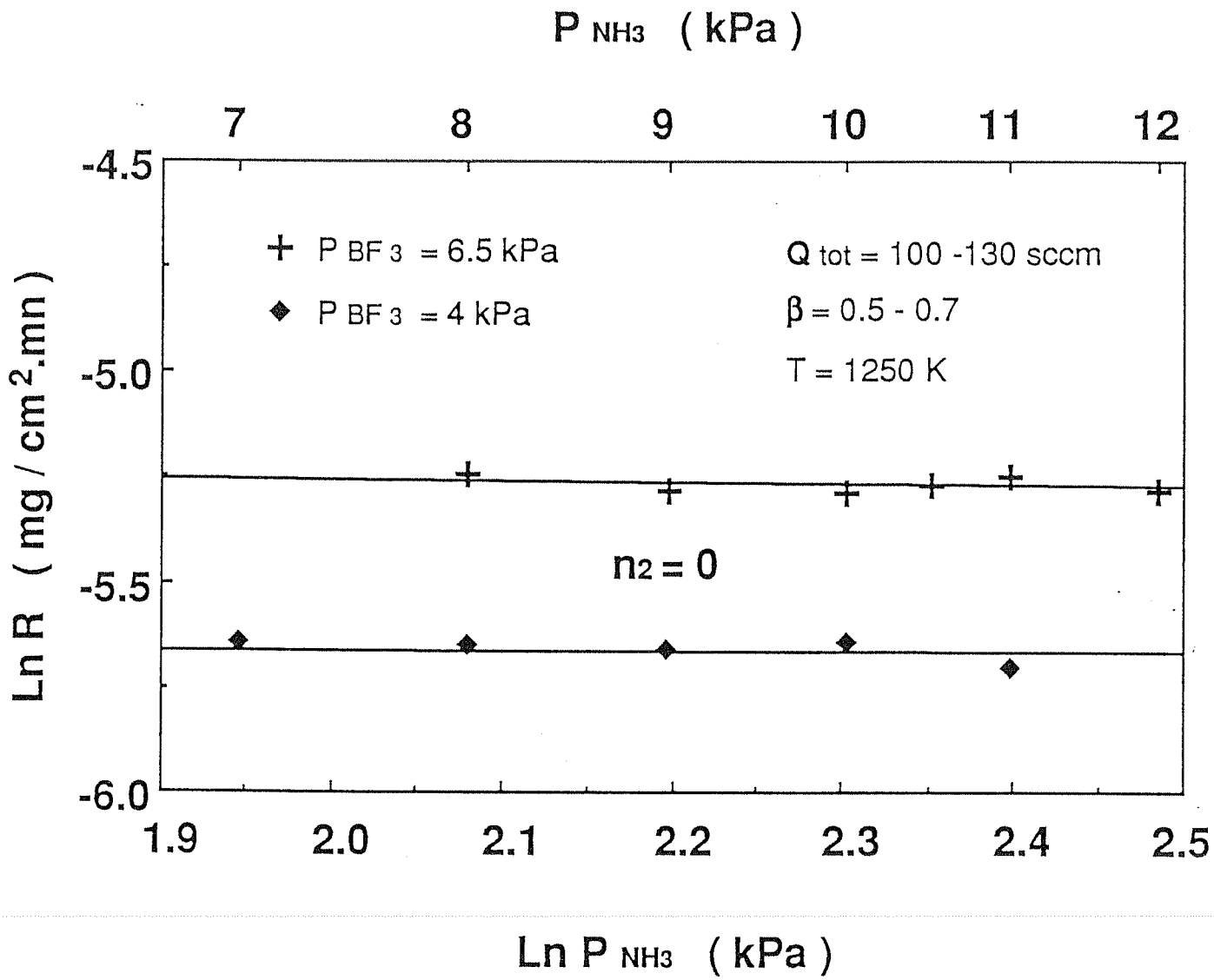

Fig.16 : Variation of BN growth rate with partial pressure of NH_3 for T= 1250 K

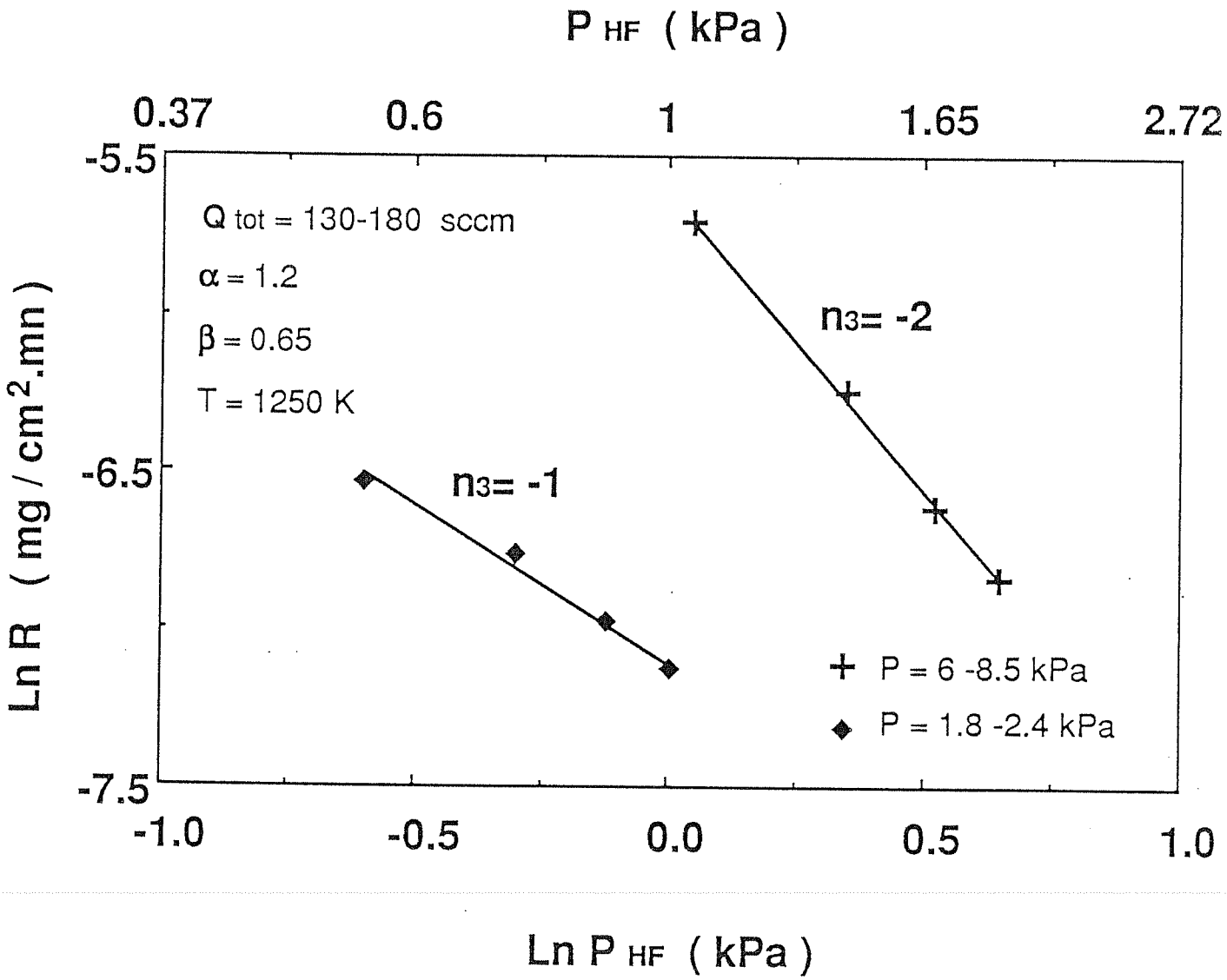

Fig.17 : Variation of BN growth rate with partial pressure of HF for T= 1250 K

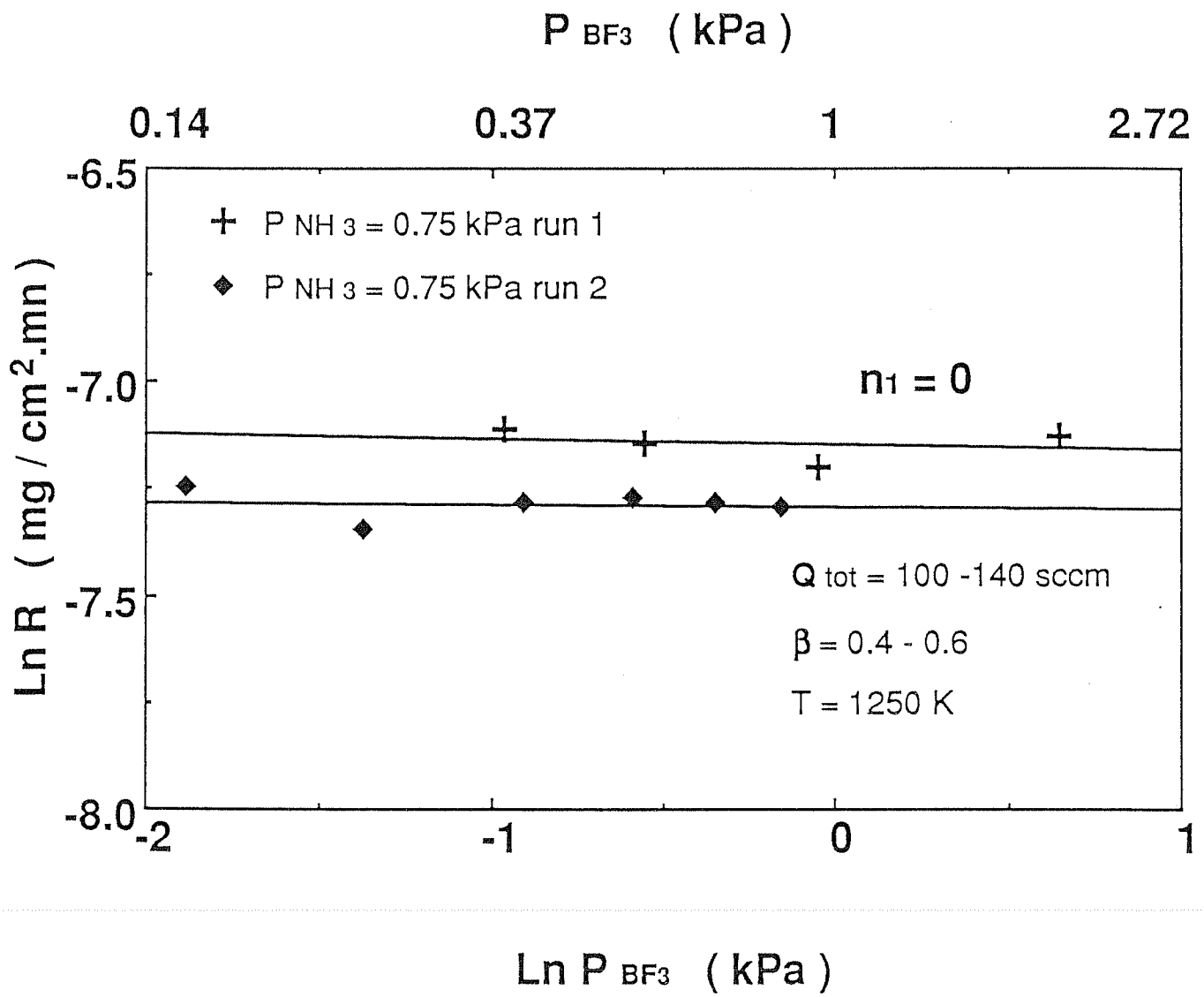

Fig.18 : Variation of BN growth rate with partial pressure of BF_3 for T= 1250 K

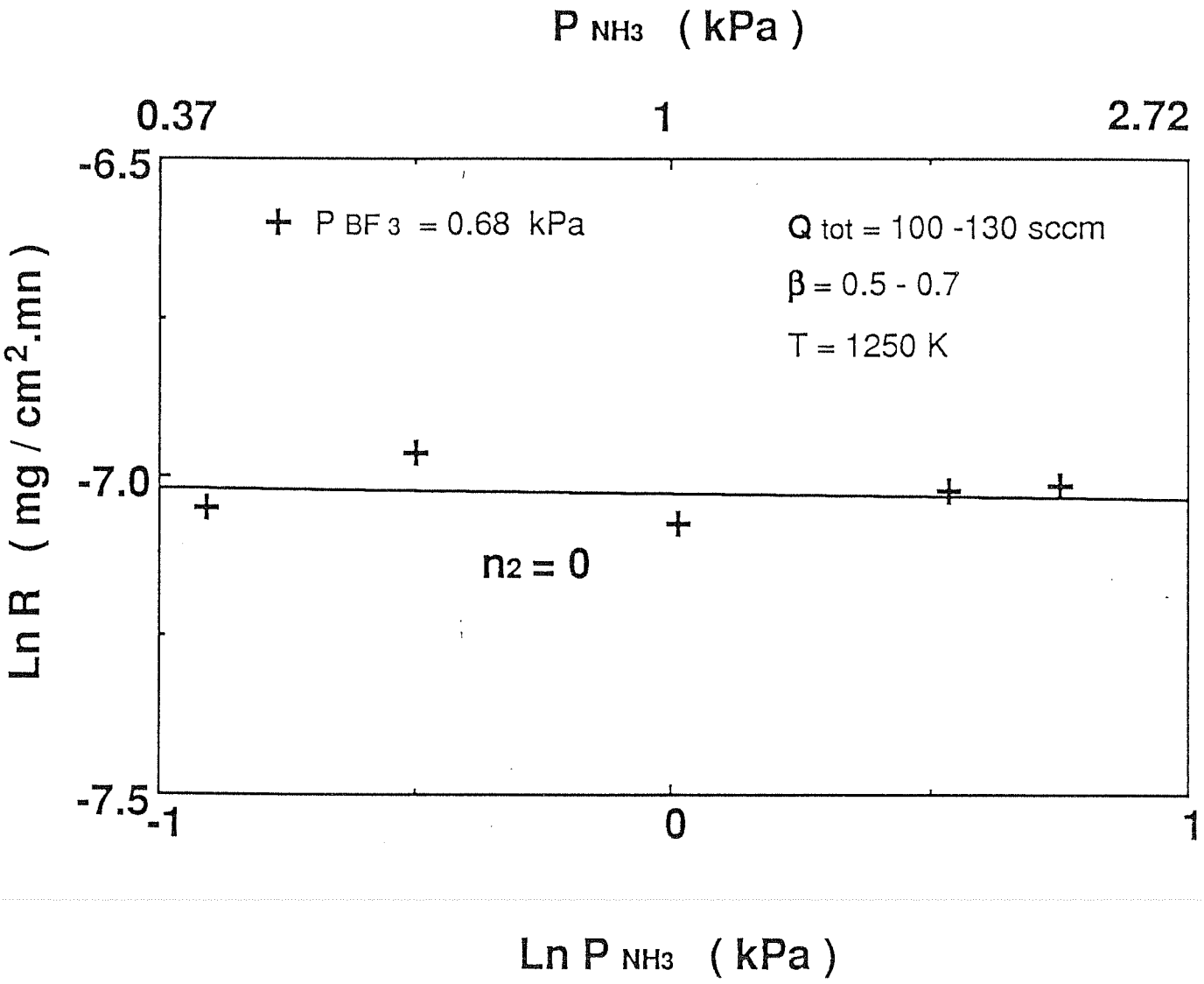

Fig.19 : Variation of BN growth rate with partial pressure of NH_3 for T= 1250 K

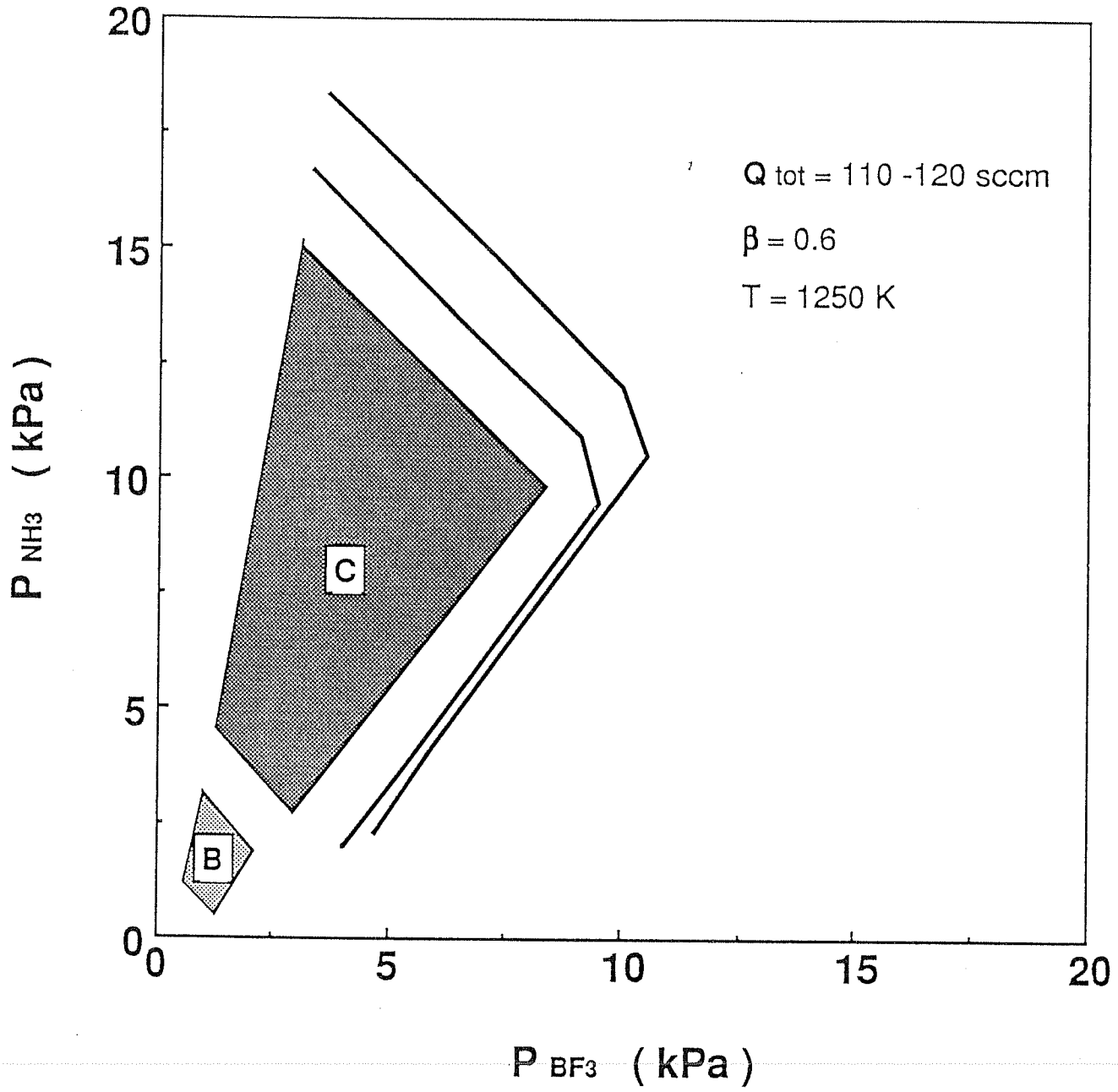

Fig.20 : Domains of validity for the kinetic laws B and C at T= 1250 K

For 1 $\leq P_{tr} \leq$ 4 kPa and 0.5 $\leq P_{HF} \leq$ 1 kPa

$R = k_0 \exp(-E_a/\Re T) [P_{BF_3}]^0 . [P_{NH_3}]^0 . [P_{HF}]^{-1} . [P_{Ar}]^0$ (Law B)

where $E_a = 100 \pm 20$ kJ mol^{-1} [11], $< k_0 > = 9.3.10^3$ mg.Pa/cm^2.mn

$< k_0 >$ is an average value calculated from all the experimental growth rates obtained in presence of added HF for 1250 K and $1 \leq P_{tr} \leq 4$ kPa

For 6 $\leq P_{tr} \leq$ 18 kPa, 1.1 $\leq P_{HF} \leq$ 2 kPa

$R = k_0 \exp(-E_a/\Re T) [P_{BF_3}]^{1.5} . [P_{NH_3}]^0 . [P_{HF}]^{-2} . [P_{Ar}]^0$ (Law C)

where $E_a = 185 \pm 15$ kJmol^{-1} [11], $< k_0 > = 5.4.10^5$ mg.Pa$^{0.5}$/cm^2.mn

$< k_0 >$ is an average value calculated from all the experimental growth rates obtained in presence of added HF for 1250 K and $6 \leq P_{tr} \leq 18$ kPa

4- DISCUSSION

The apparent reaction order with respect to argon is zero for the three temperatures and the pressure range studied. This species has been used to prevent diffusion of corrosive gases in the microbalance. It does not participate directly to the reaction of BN formation. In the considered range of β ratio, Ar does not affect the kinetic process.

The deposition rate does not depend on the initial partial pressure of NH_3, whatever the experimental conditions of temperature and pressure. Other authors have previously reported a similar result for two CVD systems where NH_3 is used as nitrogen source : BN deposited from BCl_3-NH_3-H_2 mixtures [10], and Si_3N_4 formed from $Si(CH_3)_4$-NH_3-H_2 mixtures [14]. A nil

apparent partial order in heterogeneous catalysis could be linked to a major adsorption of NH_3 or a species derived from it, *e.g.* the Lewis adduct BF_3:NH_3 (identified on the cold walls of the reactor). Therefore, two different paths are considered :

Reversible adsorption: $NH_3 + *_B <==> NH_3*$ (1)

$$\begin{cases} \text{Lewis acid-base reaction:} & NH_3 + BF_3 <==> BF_3{:}NH_3 & (2) \\ \text{Adduct physisorption:} & BF_3{:}NH_3 + (*_B\, *_N) <=> BF_3{:}NH_3{**} & (2') \end{cases}$$

where * stands for an adsorption site of the substrate surface.

Although the surface electrons are somewhat delocalized, there remains an excess of electron density on $*_N$ surface sites and a corresponding lack of electron density on the $*_B$ sites. Consequently, any N-containing molecule adsorbs preferentially on a $*_B$ site and any B-containing one on a $*_N$ site, since a B--N bond is much more energetically favored than N--N or B--B bonds. This is why equation (1) involves only $*_B$ sites and equilibrium (2') involves ($*_B*_N$) site pairs.

The choice between different kinetic laws can arise from the nature of the major adsorbed species, NH_3 or the adduct BF_3:NH_3. Adduct formation (2) is known to be a rapid reaction at low temperatures [15]. Reaction (1) should be considered at higher temperatures than reactions (2)-(2').

BF_3 species seems to play different mechanistic rôles according to the CVD conditions, as indicated by the three different partial orders 1, 1.5, and 0. The 0 order may arise from the existence of a major adsorption effect as for NH_3 ; in this case, equilibria (2)-(2') account for 0 order simultaneously for BF_3 and NH_3. These equilibria are expected at low temperatures ; indeed, partial order 0 is obtained for BF_3 at low temperatures and low pressures (law B). On

the other hand, first-order kinetics with respect to BF_3 are expected at higher temperatures, where equilibrium (1) is predominant. BF_3 can then react with the abundant NH_3* to give some intermediate adsorbed species:

– either by an Eley-Rideal (E R) mechanism :

$$NH_3^* + BF_3 \text{ <===> } BF_3{:}NH_3^* \qquad (3)$$

$$BF_3{:}NH_3^* + {}^*_N \text{ <==> } B{\equiv}N^{**} + 3\,HF \qquad (3')$$

– or by a Langmuir-Hinshelwood (L H) bimolecular mechanism :

$$BF_3 + {}^*_N \text{ <===> } BF_3^* \qquad (4)$$

$$BF_3^* + NH_3^* \text{ <===> } B{\equiv}N^{**} + 3\,HF \qquad (4')$$

The partial order 1.5 arises probably from more complex mechanisms, involving complex intermediates such as cyclic compounds and/or competition between two or more reaction paths.

The apparent partial order relative to HF is either -3, -2, or -1 depending on the conditions. Etching is not believed to occur, because even a HF-rich gas phase composition does not lead to weight loss. Explanation of negative integer orders can lie in the number of HF molecules which must be eliminated in order to obtain some critical intermediate species.

4.1- Mechanism A (T > 1300 K)

In this case, the gas phase adduct formation is not important ; on the other hand, NH_3 adsorption is predominant (Eq. (A1)). BF_3 reacts with it according to an E-R or L-H mechanism. Both paths result in the formation of

B≡N** chemisorbed intermediate and elimination of 3 HF molecules (Eq. (A2)). The remaining B≡N** adsorbed molecule is then slowly and irreversibly incorporated to the deposit network (because it probably has to migrate to a stable site (Eq. (A3)). The mechanism is summarized by the following equations:

$$NH_3 + {}^*_B \text{ <==> } NH_3{}^* \qquad \text{(A1)}$$

$$BF_3 + NH_3{}^* + {}^*_N \text{ <=> } B{\equiv}N^{**} + 3\ HF \qquad \text{(A2)}$$

$$B{\equiv}N^{**} \text{ —> } BN + ({}^*_B{}^*_N) \qquad \text{(A3)}$$

The final rate R derived from equation (A3):

$$R = k_3.[B{\equiv}N^{**}]$$

The intermediate [B≡N**] is calculated upon the assumption of quasi-steady-state regime:

$$\frac{d[B{\equiv}N^{**}]}{dt} = k_2\, P_{BF_3}\, [NH_3{}^*].\theta_N - k_{-2}\, [B{\equiv}N^{**}]\, P_{HF}^3 - k_3\, [B{\equiv}N^{**}] = 0$$

$$[B{\equiv}N^{**}] = \frac{k_2\, P_{BF_3}\, [NH_3{}^*].\theta_N}{k_3 + k_{-2}.P_{HF}^3}$$

where θ_N is the fraction of $*_N$ sites uncovered and $[NH_3{}^*]$ the fraction of $*_B$ sites covered with NH_3.

If $k_3 << k_{-2}\, P_{HF}^3$, then $[B{\equiv}N^{**}] \approx K_2\, [NH_3{}^*]\, \theta_N\, P_{BF_3}\, P_{HF}^{-3}$, with $K_2 = k_2 / k_{-2}$

Under the double assumption that $[NH_3{}^*] \approx 1$ and that $\theta_N \approx 1$ (predominant adsorption of NH_3 on $*_B$, partial orders corresponding to those actually observed (law A) are derived from the following equation :

$$R = k_3 K_2 . P_{BF_3} . P_{HF}^{-3} \qquad \text{(Eq. 1)}$$

In order to determine the influence of α on the chemical composition of the deposits prepared under the conditions of the law A, thick films of BN were synthesized, at 1450 K and P_{tr}= 1.5 kPa, on flat sintered α-SiC substrates and analysed by using an electron probe X-ray microanalyser (EPMA)[1] . The results are listed in Table 1. It was found that N/B ratios are nearly equal to the stoichiometric value when $\alpha \geq 1$.

On the other hand, when $\alpha \leq 1$ (i. e. $P_{NH_3} < P_{BF_3}$ in the initial gaseous mixture), the obtained deposit contains more boron than nitrogen in atomic percentage. The apparent reaction orders have not been determined for these α values, but this chemical composition suggests competition between two mechanisms, one conducting to BN, the other to boron containing species (i. e. oxides). The latter assumes a non-negligible BF_3 adsorption (the major species in the gaseous phase) and a decrease of NH_3 adsorption, in contradiction with the hypotheses leading to the eq. 1.

4.2- Mechanism B ($T \leq 1300$ K ; $1 \leq P_{tr} \leq 4$ kPa)

In this case, and as suggested by the partial nil orders with respect to NH_3 and BF_3, the BF_3:NH_3 adduct exists in the gas phase (Eq. (B1)) and physisorbs majoritarily on the substrate following (2') (Eq. (B2)). An intermediate stage is the formation of a chemisorbed species BF_2-NH_2 by elimination of one HF molecule (Eq. (B3)). This intermediate species is then irreversibly incorporated to the substrate, eliminating slowly and irreversibly

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[1] 75 fromCAMEBAX

α	B (% at.)	N (% at.)	O (% at.)	N / B (at.)
0.5	48.4 $\pm$ 0.5	42.1 $\pm$ 1.4	9.2 $\pm$ 1	0.87 $\pm$ 0.05
0.7	47.7 $\pm$ 0.6	42.7 $\pm$ 0.5	8.4 $\pm$ 0.4	0.89 $\pm$ 0.03
1	48.0 $\pm$ 0.7	42.4 $\pm$ 0.5	9 $\pm$ 0.2	0.88 $\pm$ 0.03
1.2	46.4 $\pm$ 0.5	44.0 $\pm$ 0.3	8.9 $\pm$ 0.3	0.95 $\pm$ 0.02
2	45.3 $\pm$ 0.5	44.8 $\pm$ 0.5	9.3 $\pm$ 0.3	0,99 $\pm$ 0.02
5	44.4 $\pm$ 0.4	43.6 $\pm$ 0.7	11.8 $\pm$ 0.7	0.98 $\pm$ 0.02

Table 1 : EPMA derived atomic compositions of the deposits for T= 1450 K, P_{tr}= 1.5 kPa, Qtot= 119 sccm and β= 0.6

two more HF molecules (Eq. (B4)). The mechanism is summarized by the following equations:

$$NH_3 + BF_3 <==> BF_3{:}NH_3 \qquad (B1)$$

$$BF_3{:}NH_3 + (*_B*_N) <==> BF_3{:}NH_3\ ** \qquad (B2)$$

$$BF_3{:}NH_3\ ** <==> BF_2\text{-}NH_2** + HF \qquad (B3)$$

$$BF_2\text{-}NH_2\ ** \longrightarrow BN + 2HF + (*_B*_N) \qquad (B4)$$

The final rate R is expressed from reaction (B4) as :

$$R = k'_4.[BF_2\text{-}NH_2\ **]$$

The intermediate $[BF_2\text{-}NH_2\ **]$ is derived upon the assumption of quasi-steady-state regime:

$$\frac{d[BF_2\text{-}NH_2**]}{dt} = k'_3\,[BF_3{:}NH_3**] - k'_{-3}\,[BF_2\text{-}NH_2**]\,P_{HF} - k'_4.[BF_2\text{-}NH_2**]=0$$

$$[BF_2\text{-}NH_2**] = \frac{k'_3\,[BF_3{:}NH_3**]}{k'_4 + k'_{-3}P_{HF}}$$

If $k'_4 << k'_{-3}\,P_{HF}$, then $[BF_2\text{-}NH_2\ **] \approx K'_3\,[BF_3{:}NH_3**]\,P_{HF}^{-1}$,

with $K'_3 = k'_3/k'_{-3}$

From equation (B2), $[BF_3{:}NH_3**]$ is determined as :

$$[BF_3{:}NH_3**] = K'_2.P_{BF_3:NH_3}\,\theta_{BN}$$

where θ_{BN} represents the fraction of pairs of sites $(*_B*_N)$ uncovered and obeys the balance equation:

$$\theta_{BN} = 1 - [BF_3{:}NH_3**]$$

with $[BF_3:NH_3^{**}]$ representing the fraction of pairs of sites ($^*B^*N$) covered by the adduct .

From the two preceding equations, $[BF_3:NH_3^{**}]$ is calculated to be :

$$[BF_3:NH_3^{**}] = \frac{K'_2.P_{BF_3:NH_3}}{1 + K'_2.P_{BF_3:NH_3}}$$

Involving the equilibrium (B1), another expression is derived :

$$[BF_3:NH_3^{**}] = \frac{K'_2.K'_1.P_{NH_3}\,P_{BF_3}}{1 + K'_2.K'_1 P_{NH_3}\,P_{BF_3}}$$

The adduct presence at the surface becomes independent of P_{BF_3} and P_{NH_3} when $K'_2.K'_1.P_{NH_3}P_{BF_3} >> 1$. Partial orders corresponding to those observed experimentally (law B) are thus obtained, as shown by the following theoritical kinetic law :

$$R \approx k'_4.K'_3.P_{HF}^{-1} \qquad \text{(Eq.2)}$$

The experiment data show that the activation energy is three times smaller in this case than in mechanism A, due possibly to the lower physisorption energy of the adduct involved here with respect to that corresponding to the chemisorption of NH_3 and BF_3.

The above mechanism is consistent with : (i) the stoichiometry of the deposits actually observed for T= 1250 K and P_{tr}= 1.5 kPa, and (ii) the reaction order with respect to BF_3 constant and equal to zero, whatever the values of α (Table 2).

4.3- Mechanism C ($T \leq 1300$ K, $6 \leq P_{tr} \leq 18$ kPa)

The noninteger partial order in BF_3 suggests the existence of more complex or intricate reaction paths. The adsorption of a majoritary NH_3-

α	B (% at.)	N (% at.)	O (% at.)	N / B (at.)
0.5	46.7 ± 1	48.0 ± 1.4	5.3 ± 1	1.03 ± 0.05
0.7	48.1 ± 0.8	49.4 ± 0.6	2.4 ± 0.3	1.03 ± 0.03
1	46.3 ± 1.9	48.2 ± 1.8	4.5 ± 0.3	1.04 ± 0.07
1.2	45.7 ± 1.6	48.5 ± 1.5	4.4± 0.5	1.05 ± 0.05
2	46.7 ± 0.3	49.3 ± 0.2	3.0 ± 0.1	1.05 ± 0.01
5	47.3 ± 1.8	49.5 ± 1.5	3.4 ± 0.3	1.04 ± 0.06

Table 2 : EPMA derived atomic compositions of the deposits for T= 1250 K, P_{tr}= 1.5 kPa, Qtot= 119 sccm and β= 0.6

containing species at the surface should be valid (NH_3 partial order is 0). Nevertheless, no complete set of equations could be properly written yet.

5- CONCLUSION

The present experimental kinetic study of the CVD of BN from BF_3-NH_3-Ar mixtures establishes the influence of the initial gas phase composition on the transition from mass tranfer to chemical reaction rate-controlled processes for three temperatures. The latter domain (in terms of P_{NH_3} ,P_{BF_3}) is significantly narrowed when (i) BF_3 becomes the major reactive species, and (ii) the temperature is increased.

In the chemical rate-controlled regime, three distinct experimental kinetic laws have been written (when $\alpha > 1$) as :

Law A

$$R = k_0 \exp(-E_a/\Re T) [P_{BF_3}]^1 . [P_{NH_3}]^0 . [P_{HF}]^{-3} . [P_{Ar}]^0$$

where $E_a = 290 \pm 15$ kJmole^{-1} and

$< k_0 > = 1.03.10^{14}$ mg.Pa^2/cm^2.mn, for T= 1450 K and $P_{tr} \leq 4$ kPa

$< k_0 > = 6.5.10^{14}$ mg.Pa^2/cm^2.mn, for T= 1350 K and $P_{tr} \leq 9$ kPa

Law B

$$R = k_0 \exp(-E_a/\Re T) [P_{BF_3}]^0 . [P_{NH_3}]^0 . [P_{HF}]^{-1} . [P_{Ar}]^0 \quad \text{(Law B)}$$

where $E_a = 100 \pm 20$ kJ mole^{-1} and $< k_0 > = 9.3.10^3$ mg.Pa/cm^2.mn

for T = 1250 K and $1 \leq P_{tr} \leq 4$ kPa

Law C

$$R = k_0 \exp(-E_a/\Re T)\,[P_{BF_3}]^{1.5}.\,[P_{NH_3}]^{0}.\,[P_{HF}]^{-2}.\,[P_{Ar}]^{0} \quad \text{(Law C)}$$

where $E_a = 185 \pm 15$ kJmole^{-1} and $< k_0 > = 5.4.10^{3}$ mg.Pa$^{0.5}$/cm^2.mn

for $T = 1250$ K and $6 \leq P_{tr} \leq 18$ kPa

Two mechanisms, accounting for these kinetic laws, are proposed to explain the chemical deposition processes of BN ; one corresponding to law A and the second to law B. The former is based on the hypothesis of a predominant NH_3 adsorption, the adsorbed species reacting with BF_3 according to Eley-Rideal or Langmuir-Hinshelwood mechanisms with the simultaneous evolution of three HF moleceules. The latter assumes the occurrence of the BF_3:NH_3 adduct in the gas phase, its physisorption on the solid and the evolution of three HF molecules in two steps.

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APPENDIX

The figure A1 represents a plane (P_{BF_3},P_{NH_3}) consituted where the coordinates of a given point are related to α and P_{tr} according to the following transformation:

$$P_{NH_3} = \frac{\alpha}{1+\alpha} P_{tr}$$

$$P_{BF_3} = \frac{1}{1+\alpha} P_{tr}$$

This transformation is merely the inverse expression of α and P_{tr} as functions of P_{NH_3} and P_{BF_3} . Any point M of coordinates (P_{BF_3} , P_{NH_3}) is characterized by a total reactive pressure equal to the sum of its coordinates ($P_{tr} = P_{BF_3} + P_{NH_3}$). The α value is given by their ratio ($\alpha = P_{NH_3} / P_{BF_3}$). All the points corresponding to the same total reactive pressure (P_{tr}) build up a segment, between M_1 (P_{tr},0) and M_2 (0,P_{tr}). A shift towards M_2 along this segment increases the α ratio. Similarly, the points corresponding to a constant α ratio form a straight line joining the origin O and M. Along this line, the total reactive pressure increases by moving away from the origin. Varying the partial pressure of one of the reactive species (P_{BF3} or P_{NH3}) corresponds to moving along a segment parallel to the appropriate axis.

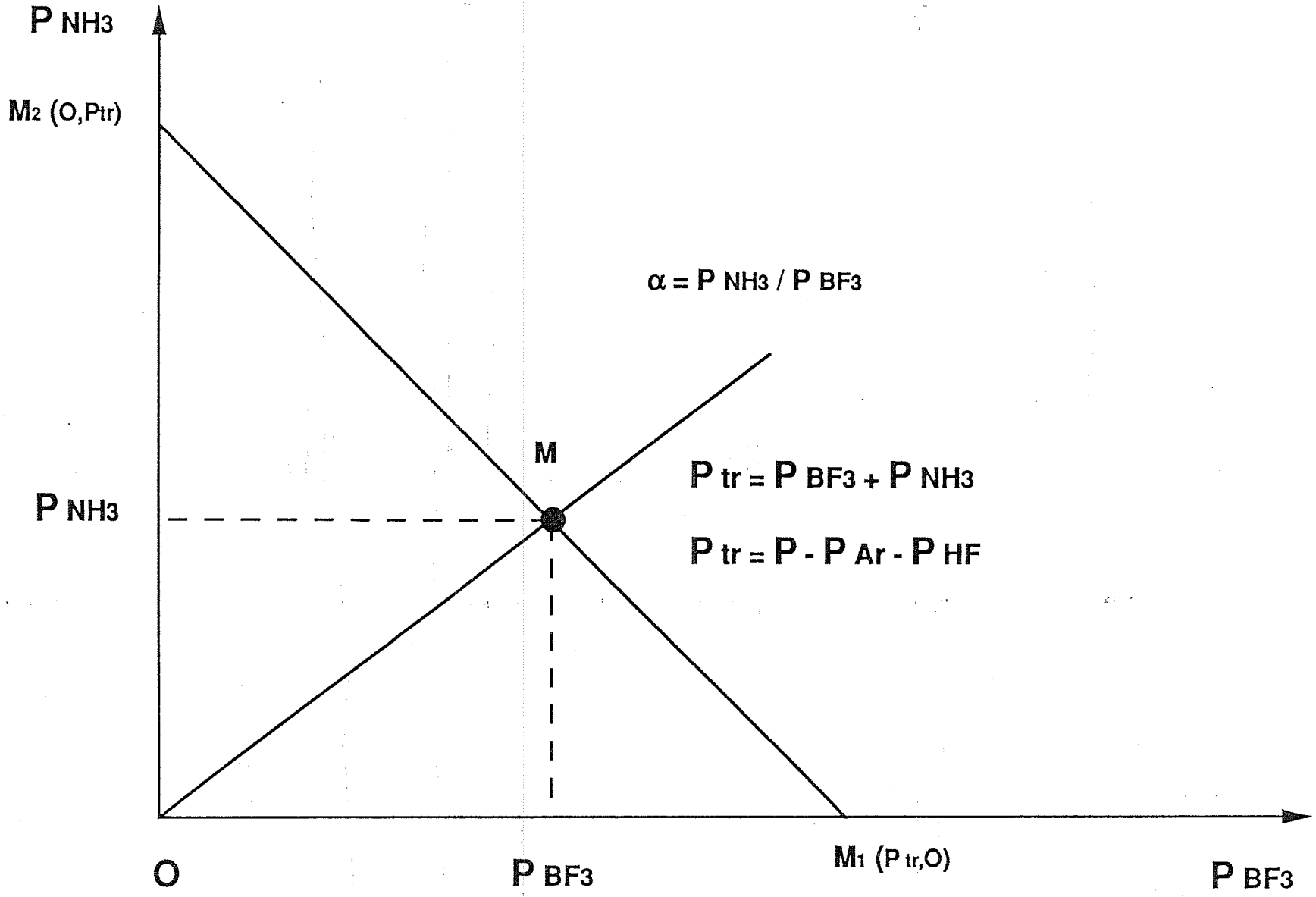

Fig.A1 : Signification of α and P_{tr} in the plane (P_{BF3},P_{NH3})